VOL. XLV 1924

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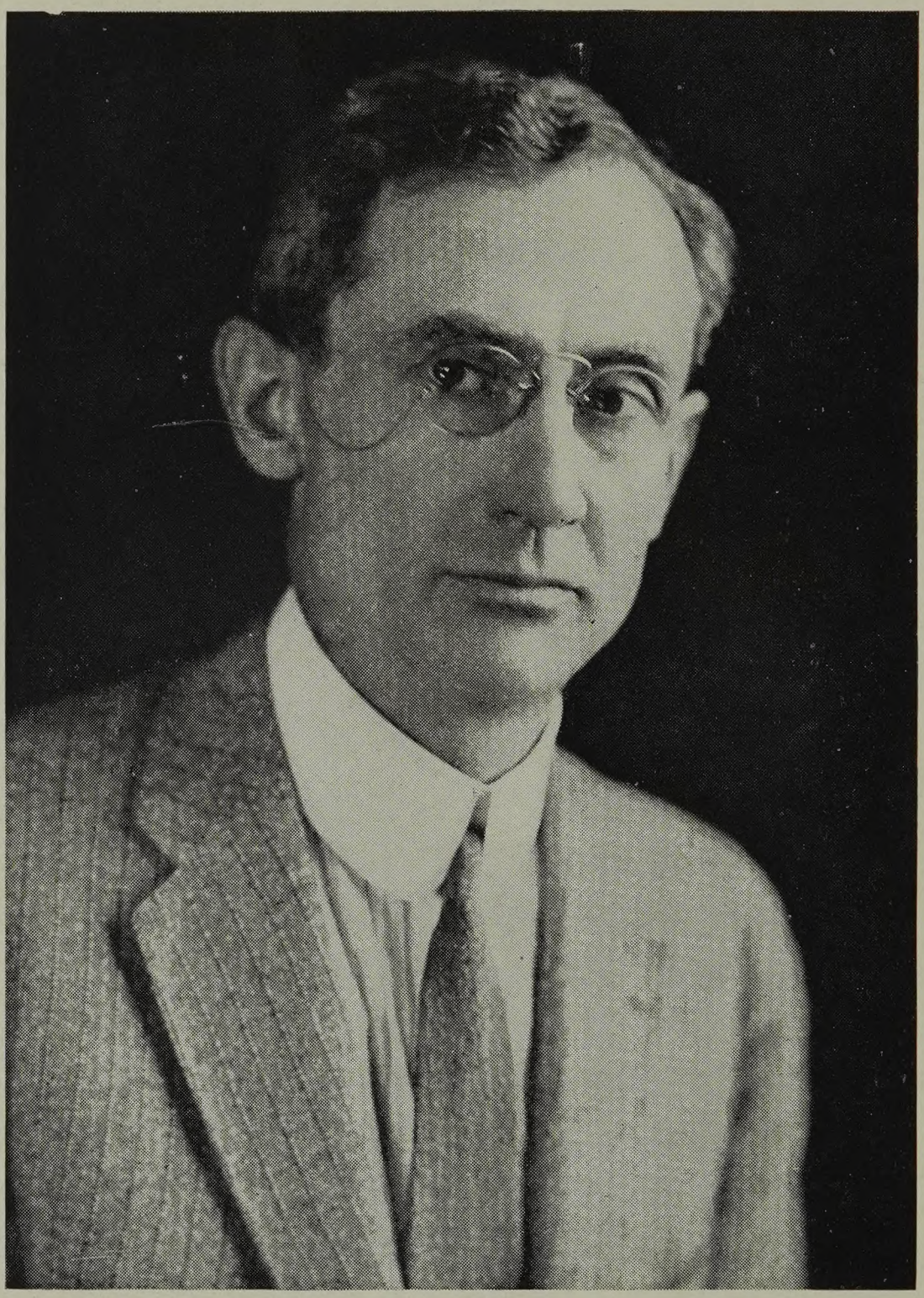

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TRANSACTIONS

OF THE

American Electrochemical Society

VOLUME XLV

FORTY-FIFTH GENERAL MEETING

PHILADELPHIA, PA.

APRIL 24, 25 AND 26, 1924

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VOLUME XLV 1924

TRANSACTIONS

OF THE

American Electrochemical Society

PROCEEDINGS

CONDENSED MINUTES AND RECORD OF THE FORTY-FIFTH GENERAL MEETING OF THE SOCIETY, HELD AT THE HOTEL BELLEVUE-STRATFORD, PHILADELPHIA, PA., APRIL 24, 25 AND 26, 1924.

The registration at this meeting was 155 members and 120 guests, or a total of 275. Registration began at 6 P. M., Wednesday, in the roof garden of the Hotel Bellevue-Stratford, where the technical sessions were held during the next three days.

PROCEEDINGS OF THURSDAY, APRIL 24, 1924

The Forty-fifth Meeting of the Society was called to order by President Hinckley at 9.30 A. M. In his opening remarks the President expressed the appropriateness of holding this meeting in Philadelphia, the birthplace of the Society in 1902. The President briefly outlined the salient points of the program of the present meeting, and then turned the meeting over to Dr. C. J. Thatcher, Chairman of the Symposium on "Organic Electrochemical Products." Dr. Thatcher introduced the symposium with a short survey of "The Present Status of Applied Organic Electrochemistry." This was followed by the presentation and discussion of papers by the following authors: Kendall S. Tesh and Alex. Lowy; Alfred R. Ebberts and Alex. Lowy; Arthur K. Doolittle; Raymond F. Dunbrook and Alex. Lowy; Fr. Fichter;

C. Schall and H. Markgraf; Masayoshi Ishibashi. All of these papers together with the discussions are printed in this volume.

At 1 P. M. the Society's members and guests attended a Round Table Luncheon at which the subject of "Refractories for Electric Furnaces" was presented and discussed with great interest and enthusiasm.

Dr. M. L. Hartmann, of Niagara Falls, made a very capable chairman. Weeks in advance he had approached various refractory manufacturers and engineers, submitting to them a long list of problems with which the refractory makers and users are confronted today.[1]

Prof. Alfred Stansfield, of McGill University, opened the discussion by presenting a general review of the conditions confronting the industry today. In his reference to the various types of electric furnaces, Prof. Stansfield confined attention mainly to the direct arc furnace and the need for better refractories. As the roofs of such furnaces are largely constructed of silica brick, which disintegrate at temperatures varying from 1,600 to 1,700° C., and as the melting point of low carbon steels is about 1,500° C., the working range between the bath and roof is not much in excess of 100°. This obviously presents an unfavorable condition, and an attempt to meet the difficulty by using a thin roof, either air or water cooled, has not proved satisfactory. A number of

[1] In electric steel furnaces:

How much of the refractory trouble is due to inadequacy of materials and how much to lack of understanding and abuse of the available materials? What is the best method for installing the magnesia hearth? What are the advantages of fused magnesia over the ordinary burnt magnesia in hearth construction? Is dolomitic refractory a satisfactory substitute for magnesite or magnesia in the hearth? In basic steel practice, is it necessary to separate the basic hearth from the silica side walls by the use of chromite? Does the introduction of electrodes through the bottoms cause any trouble in the hearth refractories? When is a carbon lining of the hearth to be recommended? Is low heat conductivity an essential requirement for roof and wall refractory materials? Under what conditions is an outer sidewall- lining of diatomaceous earth brick to be recommended? Have you ever tried water-cooling the side walls or roofs? Under what conditions and where is it advantageous to use silicon carbide refractories? Aside from high initial cost, is there any serious objection to the use of zirconia refractories in walls and roof? Have fused aluminum oxide refractories been successfully used in walls and roof? Are the high aluminous clay refractories ever used in place of silica bricks in walls and roof? What has been your experience in the use of metal cased bricks? What refractory material can be used in induction furnaces for melting iron and steel?

In electric furnaces for non-ferrous metals:

What materials and what method of installation will best prevent the penetration of metals like lead and zinc in the hearths of electrically heated furnaces? What is the principal cause of failure of fireclay refractories in induction furnaces melting high copper alloys? In melting aluminum bronze, what refractories best resist or prevent the formation of "skulls"?

foundries are now using magnesite linings with considerable success. Neutral linings of sillimanite are frequently preferred to those of silica or magnesite, but they have the disadvantages of a lower melting point and a higher electrical conductivity at elevated temperatures.

Dr. Otto Frick, inventor of the Frick induction furnace, stated that according to his experience pure magnesite makes a very satisfactory hearth lining, provided finely ground magnesite is used as a binding material. Linings of this character he found to last from three to three and one-half months. Dr. Frick was optimistic as to the adaptability of magnesite brick for roofs. He made the rather startling prediction that the operation of 100-ton electric furnaces was not far distant.

The general discussion which followed was actively participated in by electric furnace manufacturers, electric furnace users, refractory manufacturers, chemists and physicists. That an unusual amount of interest was prevalent at this Round Table may be realized from the fact that the discussion lasted for almost four hours.

Through the efforts of the Local Committee, arrangements had been made for visiting various industrial plants in the vicinity of Philadelphia. The plants which were open to inspection and the golf clubs which had kindly placed their facilities at the disposal of our members and guests are listed in the "Resolution of Thanks" on page 9.

At 6.30 P. M., the Board of Directors held its annual business meeting. The visiting ladies were the guests of the Local Committee at the theater where Jane Cowl starred in "Romeo and Juliet."

PROCEEDINGS OF FRIDAY, APRIL 25, 1924

At 9 A. M. President Hinckley opened the annual business meeting of the Society. Secretary Fink presented the annual reports of the Board of Directors and of the Secretary. These, together with the report of the Treasurer, were upon motion accepted and ordered filed. They will be found on pages 9 to 14 of these Proceedings.

Then followed the reports of the Standing Committees. Dr. Chas. F. Burgess, of Madison, Wis., chairman of the Radio Batteries Committee, called attention to the interesting fact that our Society was the first to give any recognition to the dry cell industry as a branch of the electrochemical industry. This is borne out by the publication of the first paper on dry cells, in Volume XIII of the Transactions of the Society.

Dr. George W. Vinal, a member of the same committee, presented a report of the standardization of tests for dry cells used in radio receiving sets. This report, together with the Bureau of Standards recommendations, is printed in full at the end of these Proceedings.

The next report was presented by Mr. F. A. J. FitzGerald, chairman of the Committee on Publications, and may be summarized as follows:

To the Board of Directors, American Electrochemical Society:

During the year 1923-24 your committee has received and examined 76 papers. Of these 74 were submitted for publication at the autumn meeting of 1923 and the spring meeting of 1924, while two were submitted for the autumn meeting of 1924. There were 33 papers accepted without change, 25 were accepted after revision by authors, 8 were rejected, and the balance were either returned to authors with recommendation for revision or withdrawn.

In order to give sufficient time for the examination of papers, the committee recommended that they be in their hands at least three months before the date of the meeting.

Concerning the question of papers dealing with analytical methods, the following ruling was presented by the committee for the approval of the Board of Directors:

1. Must describe an electrolytic method of analysis, or deal with analysis of a substance that enters into or is a product of an electrochemical or electrothermal process.

2. Must cover some novel method or methods or critical comparison of existing methods.

3. Must contain some actual experimental results illustrating the method.

The report was favorably received and the following is the ruling of the Board:

> That the limiting date for the acceptance of papers be definitely fixed as February 1st and July 1st, effective on and after the spring, 1925, meeting.
>
> That the recommendations of the Publication Committee concerning papers dealing with analytical methods be heartily endorsed.

In the absence of Dr. W. S. Landis, Chairman of the Fixed Nitrogen Committee, Secretary Fink presented that committee's report which in abstract is as follows:

Of the three well-known classes of fixation processes—the arc, the cyanamid and the synthetic ammonia—there is little new to add to the arc process. In regard to cyanamid plants, several of the war emergency plants discontinued operations on account of their disadvantageous location with respect to markets or raw materials. However, most of the pre-war plants in Europe are in operation and are adding to the quota of fixed nitrogen. The reception of calcium cyanamid by the European farmers has undergone a material change in the last few years with the result that the industry shows great promise of large future development. The synthetic production of ammonia is coming more into the field of the electrochemist and in a recent development is largely dependent upon electrolytic hydrogen for its successful operation. This, therefore, brings the electrochemist into contact with a process from which he was excluded in its earlier developments. The number of new plants, projected or in process of erection, for the fixation of atmospheric nitrogen, is greater than ever before, although the process is still undergoing continual improvements.

Dr. S. C. Lind's report of the Committee on Radioactivity indicated that there has been a continual decline in the radium industry in this country, for the reasons mentioned in the committee's report of last year. Although this presents a regrettable situation in the American radium industry, a reduction in the

price of radium to almost half its former value has made it more accessible for scientific and therapeutic investigations.

The report of John L. Harper, Chairman of the Water Power Committee, indicated that new customers for power for electrochemical purposes would be compelled to await the development of new power before their needs could be supplied. Unfortunately, progress in that direction has been handicapped by the refusal of governmental bodies to allow further exploitation on the Niagara and St. Lawrence Rivers.

The Chair opened and read the official

REPORT OF THE TELLERS OF ELECTION

The following is a list of votes cast in the election of officers for the year 1924-1925:

President—H. C. Parmelee, 226; A. T. Hinckley, 1.

Vice-presidents—C. F. Burgess, 197; Carl Hering, 161; F. A. J. FitzGerald, 145; A. D. Little, 113; E. L. Crosby, 58.

Managers—S. C. Lind, 189; A. H. Hooker, 177; Duncan MacRae, 140; E. A. Sperry, 101; H. S. Miner, 59.

Treasurer—F. A. Lidbury, 226.

Secretary—Colin G. Fink, 226; Carl Hering, 1.

Void ballots, 15.

(Signed) LINCOLN T. WORK,
PRESCOTT VAN HORN.

The President then announced the election of the following new officers of the Society, as the result of the Tellers' report:

President—H. C. Parmelee.

Vice-presidents—C. F. Burgess, Carl Hering, F. A. J. FitzGerald.

Managers—S. C. Lind, A. H. Hooker, Duncan MacRae.

Treasurer—F. A. Lidbury.

Secretary—Colin G. Fink.

Following this announcement the Chair requested Mr. Howard to escort President-elect Parmelee to the platform. After ex-

pressing his gratitude for the honor conferred upon him in his familiar eloquent style, Dr. Parmelee assumed the Chair while the retiring President, A. T. Hinckley, delivered an address on "The Service Rendered by Technical Societies."* Following this, the Chair turned the meeting over to S. Skowronski, of Perth Amboy, N. J., and his symposium on "Recent Progress in Electrodeposition." Mr. Skowronski called upon Dr. Wm. Blum, of Washington, to introduce the subject of electroplating and electroforming. This was followed by the reading and discussion of papers by the following: C. T. Thomas and W. Blum; L. D. Hammond; C. P. Madsen; V. Kohlschütter; G. H. Montillon and N. S. Cassel; C. J. Wernlund; F. F. Farnsworth and C. D. Hocker; E. M. Baker and Richard Schneidewind. All of these papers, with discussions, are printed in this volume.

At 12.30 P. M. the members and guests attended an informal Round Table discussion on "Future Progress in Electrodeposition," at which Mr. Skowronski also presided. In order to utilize to best advantage the time available for this meeting the discussion was divided into four groups with the following headings: Educational institutions, research laboratories, works laboratories and plant operation. Dr. H. S. Lukens, of the University of Pennsylvania, and Prof. M. deK. Thompson, of the Massachusetts Institute of Technology, stressed the important functions which the University research laboratories play at the present time. Prof. Thompson mentioned that it has been necessary in many research problems to continue the work from one year to the next on account of the limited number of hours at the disposal of the individual student.

Floyd T. Taylor, of A. P. Munning & Co., Matawan, N. J., followed up the discussion by saying that research should be carried out on a commercial scale so as to avoid the very general criticism of "it may be all right in theory, but it does not work in practice." W. E. Hughes, of England, in a written communication, strongly recommended that efforts be directed toward better co-operation and understanding between the practical and scientific man, and as one step nearer this goal suggested that laboratory results be presented to the electroplater in the shop in plain, understandable terms. He predicted great future develop-

* See page 27 of this volume.

ments in the deposition of the metals manganese and chromium, as well as improvements in the commercial processes for the refining and extraction of metals.

C. P. Madsen very interestingly related some of his experiences in the electroforming of nickel tubes, sheets, etc., pointing out that tubes can be produced up to a thickness of ⅛ inch at a cost which compares favorably with the old extrusion process.

At 2 o'clock the technical meeting adjourned and the members took in a delightful boat ride up and down the Delaware, stopping at the government air craft plant. The boat returned to Camden at 5.30 P. M., from whence the party took the train to Morris-on-the-Delaware where a most excellent planked shad dinner was served at Kugler's Old Mohican Club. The evening was brought to an enjoyable close by a very illuminating illustrated lecture on "The Atom" by John Mills, of the Western Electric Co.

PROCEEDINGS OF SATURDAY, APRIL 26, 1924

The meeting convened at 9 A. M. The first paper of the morning was presented by E. R. Berry, who had also placed on exhibition some samples of his clear fused quartz.

Then the symposium of Friday morning was continued, and accordingly the meeting was again turned over to Mr. Skowronski, who opened this second part of the symposium by briefly recounting "The Improvements Made in Electrolytic Refining During the Last Decade." The following authors presented papers: H. Y. Eagle; C. W. Eichrodt; Edward F. Kern and Edward A. Capillon; Charles L. Mantell; J. R. Stack; Donald Belcher; B. S. Hopkins and A. W. Meyer; E. A. Engle and B. S. Hopkins; C. A. Mann and H. O. Halvorsen; Cleveland F. Nixon; and Alfred L. Ferguson and Gerrit Van Zyl.

All of these papers and discussions are printed in these Transactions. There is also included the paper of Prof. Chas. Kraus (Nichols medalist), which he had presented at a meeting of the New York Section of the Society. The paper is entitled, "The Properties of the Elements in the Electronegative Condition." In concluding the technical program, President Hinckley, on behalf of the Society, thanked both Mr. Skowronski and Dr.

Thatcher for their most valuable assistance in arranging and conducting the two very successful symposia.

Prior to adjourning this forty-fifth meeting of the Society, R. H. White presented the following

RESOLUTION OF THANKS

Resolved, That the American Electrochemical Society at its forty-fifth meeting, held in Philadelphia, April 24, 25 and 26, 1924, hereby expresses its thanks to the following for their kindness in entertaining the members:

The Department of Docks, Wharves and Ferries of the City of Philadelphia, and specifically to the Director, George F. Sproule, for the loan of the boats for the boat trip.

To the League Island Navy Yard, and specifically to the Commandant, Admiral Scales, for the inspection of the Aircraft Plant.

To the Edgewood Arsenal for the invitation to the demonstration on Saturday, April 26th.

To Mr. John Mills for his very entertaining and instructive lecture on "The Atom" at the Shad Dinner.

To the following for inviting members to visit their plants:
Ajax-Wyatt Company,
Brown Instrument Company,
Disston Company,
Dodge Steel Castings Company,
Keasby & Mattison Company,
Welsbach Company.

To the Penn Athletic Club and the Golf Club for inviting members to their grounds for trap shooting and golf.

To the local committee and the ladies' committee.

ANNUAL REPORT OF THE BOARD OF DIRECTORS

To the members of the American Electrochemical Society:

The following are some of the important items of business transacted by your Board of Directors during the past year:

Dr. Edward G. Acheson was elected by a unanimous vote to Honorary Membership in the Society at its spring meeting.

An amendment to "Rulings of the Board" was passed in the

following form: *Resolved,* That papers may be accepted by the Publication Committee in cases where, in the opinion of the Board, such papers are desirable for the complete treatment of a symposium subject.

It was moved and carried that the Chairman of a symposium shall automatically become a member of the Publication Committee for the period preceding the date of that particular meeting.

In order to restrict the size of the Society's bound Transactions, as well as to serve as a precedent for the Publication Committee in considering papers submitted to the Society, the Board passed the following amendment to the "Rulings of the Board": That the Publication Committee limit the number of papers for a given meeting in accordance with the number of pages allowed in the volume.

In order not to have any papers held over for publication in Volume XLV (Philadelphia meeting), the Board authorized the Publication Committee to exceed the 400-page limit in Volume XLIV so as to bring the publication of papers in volumes up to date.

The following ruling was adopted pertaining to manuscripts submitted to the Society in the name of a company research staff: That if possible, at least one name of an individual be attached to papers submitted to the Society in the name of a company research staff, and that the Publication Committee secure such names, if possible, as well as determine the acceptability of the paper.

In order to profit by a discount of 25 per cent (instead of a former 10 per cent) on engraving work, the Society has placed its orders with the H. C. Jones Engraving Co. since September, 1923.

The Board approved the idea of a "chlorine scholarship," and appointed Acheson Smith a committee of one to investigate the feasibility of establishing such a scholarship in the Society.

In order to fix the dates of future meetings of the Society and thus to avoid conflicting with the dates of other societies, the Board, at its May meeting, took the following action: *Resolved,* That hereafter the spring meetings of the Society will be held on

the last Thursday, Friday and Saturday of April, unless these days fall within Holy Week, in which case the meeting will be held the week following. It was further *Resolved,* That the fall meetings of the Society be held on the last Thursday, Friday and Saturday of September, unless the Board rules otherwise. (The Secretary had been previously instructed to confer with the secretaries of all important allied technical and scientific societies, and to select dates which did not conflict with the dates of these other societies.)

SECRETARY'S ANNUAL REPORT

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN:

During 1923 the Society held two General Meetings—one in New York City, May 3, 4 and 5, at which the attendance was 168 members and 86 guests, total 254; the second in Dayton, Ohio, September 27, 28 and 29, at which the registration was 88 members and 102 guests, total 190. The spring meeting was featured by two symposia—"Electrode Potentials" and "The Production and Application of the Rarer Metals"—and included the presentation of 30 papers for discussion. At the fall meeting 29 papers were presented for discussion, the feature of the technical program being the symposium on "Electrochemistry of Gaseous Conduction."

The following bound Transactions of the Society have been mailed to members of the Society since its last annual meeting:

Volume XLIII, New York Meeting, in September, 1923.
Volume XLIV, Dayton Meeting, in February, 1924.

In other words, the distribution of volumes is up to date and the next volume to be issued will cover the transactions of this Philadelphia meeting. The editions of the two volumes mentioned above were as follows:

Volume No.	Copies complete bound in cloth	Copies bound in paper for Faraday Society	Copies for Storage	Free copies of each paper to authors
XLIII	1500	50	100	10
XLIV	1500	100	100	10

The stock of volumes on hand January 1, 1924, was as follows:

Volume I, 63; II, 101; III, 9; IV, 185; V, 208; VI, 180; VII, 168; VIII, 301; IX, 315; X, 259; XI, 268; XII, 264; XIII, 271; XIV, 350; XV, 340; XVI, 399; XVII, 559; XVIII, 585; XIX, 426; XX, 362; XXI, 419; XXII, 429; XXIII, 345; XXIV, 464; XXV, 487; XXVI, 478; XXVII, 225; XXVIII, 473; XXIX, 86; XXX, 418; XXXI, 71; XXXII, 315; XXXIII, 276; XXXIV, 256; XXXV, 376; XXXVI, 542; XXXVII, 564; XXXVIII, 455; XXXIX, 924; XL, 596; XLI, 746; XLII, 673; XLIII, 814.

Condition of Membership of the Society in 1923.

Members, January 1, 1923	1,961	
Qualified as members in 1923	99	
Reinstated as members in 1923	8	
		2,068
Deaths in 1923	9	
Resignations in 1923 (to date Feb. 21, 1924)	75	
Dropped by request	16	
Dropped for non-payment of 1922 dues	204	
		304
Members, January 1, 1924		1,764
Net decrease for calendar year		197

Condition, April 15, 1924.

Members, January 1, 1924	1,764	
Qualified as members	28	
Reinstated	1	
		1,793
Deaths	1	
Resignations	8	
Dropped for non-payment of 1923 dues	118	
Dropped by request	3	
		130
Members, April 15, 1924		1,663
Members, May 1, 1923		1,784
Net decrease		121

Financial Statement.

The following is a statement of receipts and expenditures as of December 31, 1923:

Receipts in 1923

Cash Balance—January 1, 1923		$ 6,052.98
Entrance Fees	$ 375.00	
Dues, 1923	9,580.26	
Dues, 1922	898.22	
Dues 1921	14.90	
Dues, 1924	3,155.00	
Dues, 1925, 1926, 1927	24.00	
Volumes—1921	5.00	
Volumes—1922	603.97	
Volumes—1923	3 009.65	
Volumes—1924	1,140.00	
Volumes—1925, 1926, 1927	15.00	
Sale of Publications	3,299.92	
Sale of Reprints	622.57	
Sale of Preprints	217.83	
Sale of Membership Certificates	10.00	
Sale of Society Pins	85.00	
Payment from Faraday Society	120.26	
Subscriptions to Faraday Soc. Trans.	601.00	
New check for one protested	18.00	
Interest on Bank Balances	161.25	
Interest on Bonds	32.02	
Refund from meeting appropriations	85.03	
Miscellaneous (overpayments, etc.)	23.60	
Total Receipts, January 1 to December 31, 1923		24,097.48
Bank refund on check collection charge		.24
Total		$30,150.70
Total Disbursements		23,985.43
Cash Balance, December 31, 1923		$6,165.27

Expenditures in 1923

Publication Expenses:

Printing of Volume 41	$ 2,078.22	
Printing of Index to preprints and disc. (Vol. 41)	19.25	
Printing of Volume 42	1,728.40	
Printing of Index to preprints and disc. Vol. 42)	19.25	
Printing of preprints (43d Meeting)	2,929.62	
Printing of Volume 43	2,194.27	
Printing of Discussions (43d Meeting)	376.76	
Printing of Preprints (44th Meeting)	2,349.38	
Engraving	621.60	
Extra Reprints	452.56	
"Suggestions to Authors" booklet	44.50	
Total Publication Expenses		$12,813.81

Office and General Expenses:

Secretarial Appropriation	$ 4,200.00	
Office Printing	888.72	
Office Postage	88.14	
Postage on Preprints and Bulletins	760.62	
Postage on Volumes	415.41	
Freight and Express on Volumes and Preprints	55.08	
Expenses of Meetings	1,166.28	
Membership Certificates	3.44	
Membership Committee	134.48	
Publication Committee	89.55	
Local Sections	225.00	
Electrothermic Division	3.00	
Electrodeposition Division	2.25	
Office Equipment	169.39	
Office Expense, Stationery, Supplies, etc.	546.89	
Storage and Insurance	352.48	
Total Office and General Expenses		$ 9,100.73
Total Expenditures—January 1 to December 31, 1923		$21,914.54
Purchase of U. S. Treasury Certificates		2,026.43
Refund, collection charges on checks and protested checks		44.46
Total Disbursements		$23,985.43

TREASURER'S ANNUAL REPORT, 1923

January 1, 1923, Cash Balance	$ 6,052.98	
Total Receipts, 1923	24,097.72	
		$30,150.70
Total Expenditures		21,914.54
		$8,236.16
Cost of U. S. Treasury Certificates	$ 2,026.43	
Collection Charges on checks, refund on overpayment, etc.	44.46 *	
		$ 2,070.89
Balance, December 31, 1923		$ 6,165.27
Balance in Power City Bank, December 31, 1923	$ 6,581.09	
Deposits not included in bank statement	617.60	
Balance retained as petty cash by Secretary's office	50.00	
		$ 7,248.69
Less December, 1923, checks not in		1,083.42
Balance, December 31, 1923, as above		$ 6,165.27

F. A. LIDBURY,
Treasurer.

AUDITORS' REPORT

We have examined the above statements of accounts, receipts and expenditures for the year 1923 and find the same to be correct.

(Signed) HARRY WOLF,
E. F. CONE,
Auditors.

* Remittance of $4.80 deducted (signature missing) and refunded, not taken into account, as total receipts of $24,097.72 include this amount.

REPORT OF RADIO BATTERY COMMITTEE ON THE STANDARDIZATION OF TESTS FOR DRY CELLS USED IN RADIO RECEIVING SETS

The committee, consisting of the undersigned, was appointed to undertake the standardization of tests for radio batteries. Two meetings of the committee have been held, the first at Washington, on November 26, 1923, and the second at Cleveland, February 25, 1924. The recommendations of the committee are based on a large amount of experimental work on various makes of dry batteries that have been tested in the laboratories of several manufacturing companies and at the Bureau of Standards during the past year.

Two types of batteries for radio service have been considered. These may be designated as the filament or "A" battery, and the plate or "B" battery. The former consists of cells capable of efficiently supplying current up to 0.25 ampere for heating the filament of vacuum tubes, and the latter consisting of 15 or more cells connected in series to supply the required potential difference between the filament and the plate, the current being a few milliamperes.

The committee is of the opinion that intermittent tests which approximate the conditions of service of the "A" batteries are to be preferred to continuous tests, although the latter can be made more quickly. Three factors are of importance in determining the character of the tests to be specified for these batteries: (1) The average weekly use of radio sets; (2) the current drain on the cells in its relation to their maximum service efficiency; and (3) the cut-off voltage.

Information about the weekly use of batteries for radio sets during summer and winter months was obtained from various parts of the country by the National Carbon Company. Fig. 1 is a summary of the data. It indicates an average weekly use of the batteries of 15 hours in summer and 23 hours in winter. The tests which are recommended, therefore, include, respectively,

discharge periods of 2 and 4 hours per day corresponding to 12 and 24 hours per week.

The current requirements for tubes adapted for use with dry cells are ordinarily about 0.06 and 0.25 ampere per tube, as indicated in Table I, giving data for the more common types. Preliminary experiments on which the recommended tests were based included discharges at various current rates between 0.06 and 0.50 ampere.

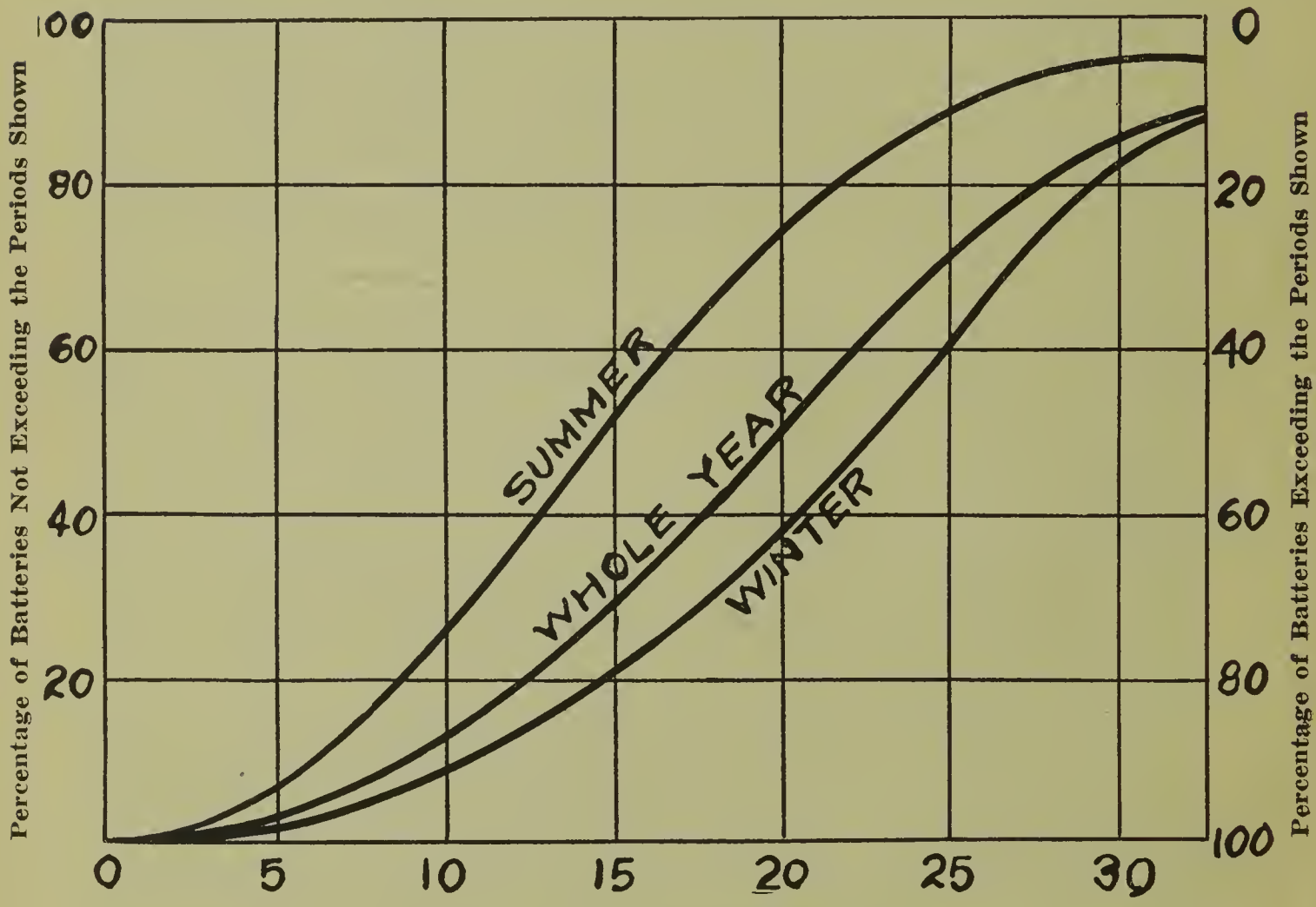

Fig. 1. Weekly Use of Batteries for Radio Sets.

The committee recommends current drains as follows: (a) 0.125 ampere, which corresponds to a single series of cells supplying current for two of the 0.06 ampere tubes or two cells in multiple supplying current for a 0.25 ampere tube; and (b) 0.25 ampere, which represents the condition of a single series of cells, supplying current to four of the 0.06 ampere tubes or one 0.25 ampere tube. These are the combinations of cells recommended by most battery manufacturers.

The rated voltages for the various tubes as indicated in the data table are shown to be either 1.0 or 1.1 volt per cell (3 cells in series being used on the 3.0 volt tubes), but experience has shown that most of these tubes can be used with reasonable efficiency down to 0.9 volt per cell. The cut-off voltage for the tests recommended has therefore been set at 0.9. New types of dry cells developed recently for radio filament circuit use, com-

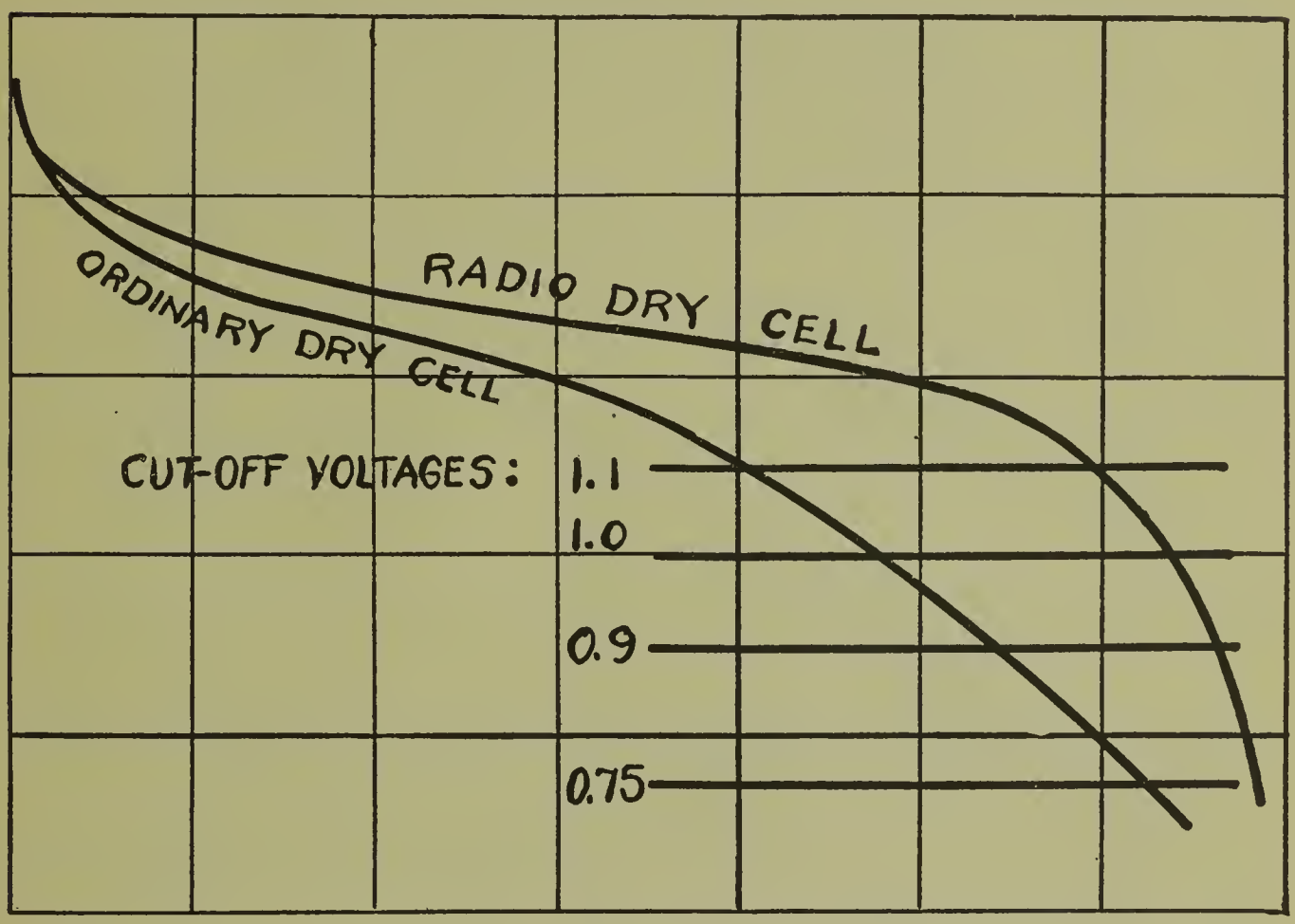

Fig. 2. Comparison of Discharge Curves of Radio Dry Cells and Ordinary Dry Cells. (Intermittent discharge at constant current.)

pared with the ordinary dry cell, are capable of maintaining a higher voltage throughout their life, followed by a much more rapid dropping off of the voltage when exhausted. This characteristic, which is particularly valuable for radio service, is shown in Fig. 2. This characteristic makes the exact value of the cut-off voltage of relatively little importance.

Additional reasons for selecting these particular combinations of conditions were based on the fact that the former represents average light use conditions, and is on the upward slope of the

service efficiency curve, and the latter represents average heavy service conditions and is on the downward slope of the efficiency curve. The relation of these two tests to the cell efficiency is shown in Fig. 3. The point of maximum capacity for the 4-hour discharge per day appears to be at about 0.1 ampere, and for a 2-hour daily discharge at about 0.2 ampere.

TABLE I.

Vacuum Tubes for Use with Dry Cells.

Vacuum Tube	Voltage	Current
WD 11	1.1	0.25
WD 12	1.1	0.25
UV 199	3.0	0.06
UV 201A	5.0	0.25
C 301 A	5.0	0.25
DV 2	5.0	0.25
DV 3	3.0	0.065
DV 3 A	3.0	0.065
Sodion	3.0	0.25

RECOMMENDED TESTS FOR FILAMENT BATTERIES ("A" BATTERIES).

1. Heavy service test. Not less than 3 cells of each kind connected in series are discharged at a constant current of 0.25 ampere for a continuous period of 4 hours on each of 6 days per week, with intervals of not less than 16 hours intervening between the discharge periods.

The following readings will be taken:

Initial open-circuit voltage.

Initial closed-circuit, or working, voltage.

Closed-circuit voltage readings at the end of each discharge period.

The test is considered completed when the closed circuit voltage at the end of a period of discharge falls below 0.9 volt per cell. The test is reported as the hours of actual discharge to this cut-off voltage.

2. Light service test. Not less than 3 cells of each kind connected in series are discharged at a constant current of 0.125

ampere for a continuous period of 2 hours on each of 6 days per week, with intervals of not less than 16 hours intervening between the discharge periods.

The following readings will be taken:

Initial open-circuit voltage of the battery.

Initial closed-circuit, or working, voltage.

The closed-circuit voltage at the end of the third and sixth discharge period of each week.

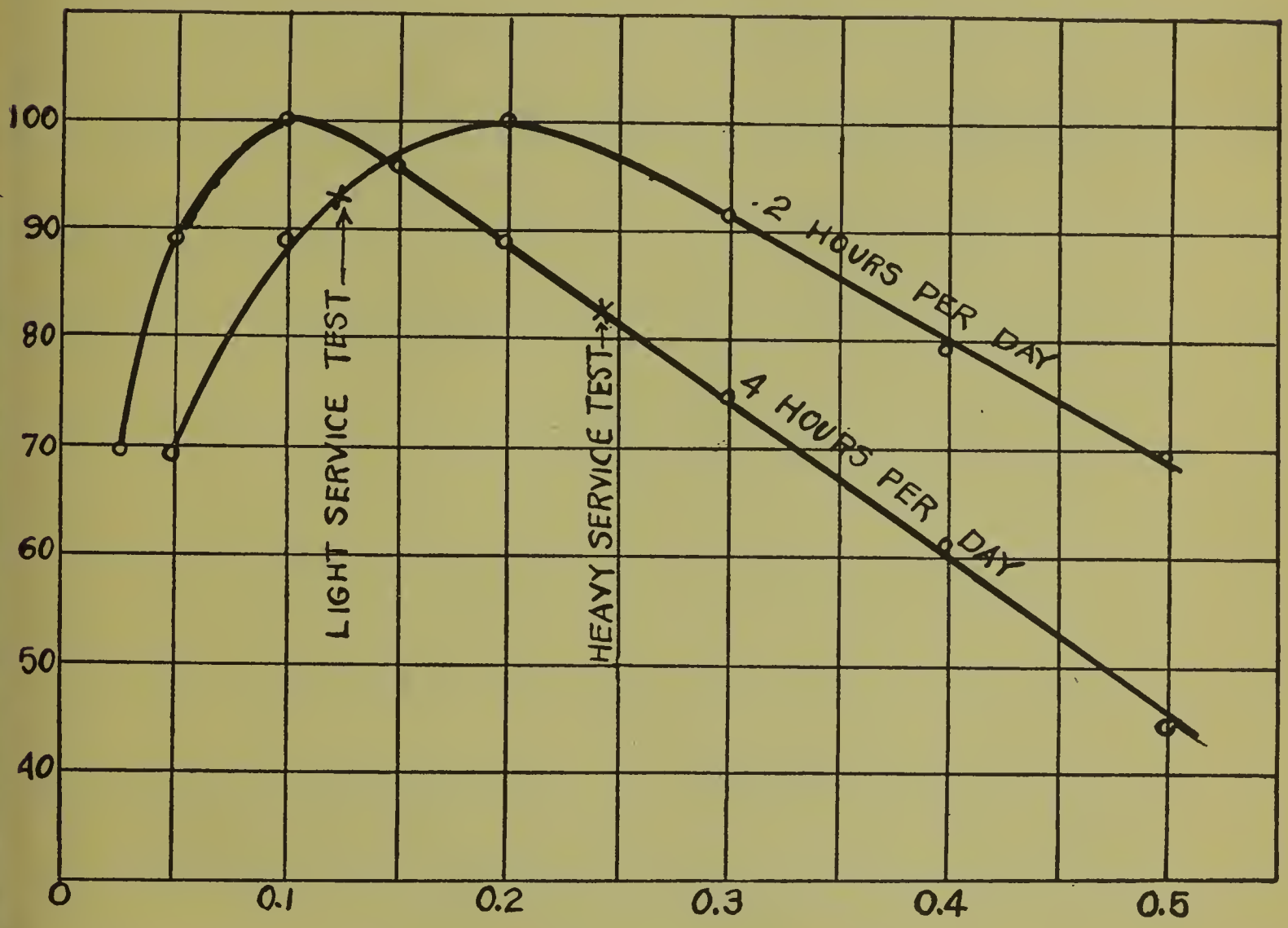

Fig. 3. Relation of the Tests to the Maximum Service Efficiency of the Cells.

The test is considered completed when the closed circuit voltage at the end of a period of discharge falls below 0.9 volt per cell. The test is reported as the hours of actual discharge to this cut-off voltage.

Note: When this test is used for cells smaller than 6 by 15 cm.

(2½ by 6 in.), it will be necessary to take closed-circuit readings at the end of each period.

TESTS FOR PLATE BATTERIES ("B" BATTERIES).

The tests to be specified for plate batteries ("B" batteries) should be for the 15-cell, 22.5 volt unit, irrespective of the size of cells contained. It was decided to specify two tests, one the continuous 5,000-ohm test, substantially as given on page 8 of Bureau of Standards Circular 139, U. S. Government specification for dry cells, and also to specify an intermittent 5,000-ohm test to cover the shelf life factor. These tests were specified for batteries containing 15 cells, regardless of size (nominal voltages of the battery 22.5 volts), and were as follows:

1. 5,000-ohm continuous test. The batteries are discharged continuously through 5,000 ohms per battery until the closed circuit voltage of the battery has fallen below 17 volts.

The following readings will be taken:

Initial open-circuit voltage.

Initial closed-circuit voltage.

Closed-circuit voltages twice daily for the smallest size and similar readings daily for intermediate and large sizes.

The results of this test are reported as the number of hours of discharge to the cut-off voltage.

2. 5,000-ohm intermittent test. The batteries are discharged through 5,000 ohms for a continuous period of 4 hours on each of 6 days per week with intervals of not less than 16 hours intervening between the discharge periods.

The following readings will be taken:

Initial open-circuit voltage.

Initial closed-circuit, or working, voltage.

Closed-circuit voltage readings at the end of the third and sixth discharge period of each week, except for readings of the smallest size of battery, which are to be made daily.

This test is considered completed when the closed-circuit voltage

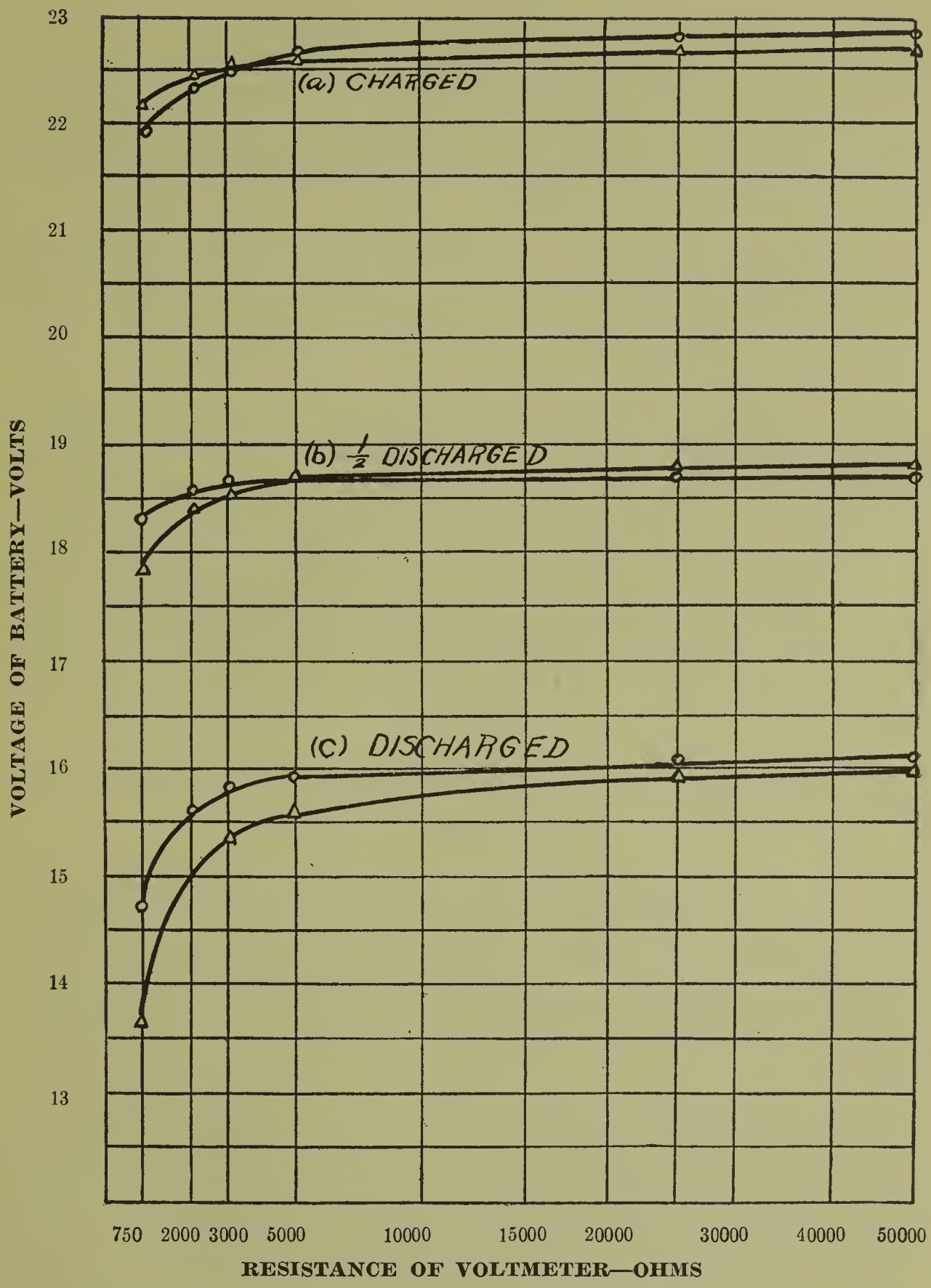

Fig. 4. Curves showing the variation of voltage readings of two standard makes of "B" Batteries when measured with voltmeters ranging in resistance from 750 to 50,000 ohms.

at the end of a period of discharge falls below 17 volts. The result of this test is reported as the number of hours of actual discharge to the cut-off voltage.

INSTRUCTIONS FOR TESTING.

1. Voltage. The voltage of individual cells for the filament circuit shall be measured with a voltmeter having a resistance of not less than 100 ohms per volt, and having not less than 50 divisions per volt on its scale.

The voltage of batteries for the plate circuit shall be measured with a voltmeter having not less than 50,000 ohms resistance, and a scale of not less than 5 divisions per volt, readings being estimated to 0.1 volt.

If a voltmeter conforming to the above quality is not available, voltmeters of lower resistance may be used to obtain approximate values. The error introduced will depend upon the resistance of the voltmeter and the condition and size of the cells in the battery. A voltmeter having 5,000 ohms resistance, for example, may give indications by as much as 10 per cent below the true value when used to measure a battery containing cells 32 by 57 mm. (1.25 by 2.25 in.) This error may be increased on cells of smaller size.

2. Temperature. The standard temperature for making tests is 20° C. Deviations from this must be stated.

The committee presents data to show the necessity for using high resistance voltmeters in determining the cut-off voltages for these batteries. As a result of the discussion on this point, it was decided to include in the specification a description of the type of voltmeter required for making accurate tests of "B" batteries. See Fig. 4.

Data presented by one manufacturing company indicated a close agreement between the results of the intermittent discharges of the large size "B" batteries, and the continuous discharges through 5,000 ohms for batteries having a satisfactory shelf life.

It was agreed that the tests for radio "A" batteries could be considerably simplified by providing for discharges of the cells through fixed resistances instead of discharges at constant current. No information was available to show what these resistances should be, and the committee felt it necessary therefore to specify that the tests be made at constant current. At some later time it may be desirable to change this procedure if it is found possible

to select fixed resistances for the discharge circuits, which will give results comparable to those obtained from the tests now in use.

A report of the work of this committee was made to the battery committee of the Associated Manufacturers of Electrical Supplies in New York on November 7, 1923. The tests recommended were adopted by them.

C. F. BURGESS,
C. A. GILLINGHAM,
G. W. VINAL.

NOTE: The Bureau of Standards, Geo. K. Burgess, Director, adopted, on April 28, 1924, the following minimum requirements for the tests outlined in the above report:

For the light service test, 200 hours.
For the heavy service test, 90 hours.

MEMBERS AND GUESTS REGISTERED AT THE FORTY-FIFTH GENERAL MEETING

Members

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E. M. Baker
A. T. Baldwin
R. L. Baldwin
Edwin W. Beardsley
E. A. Beck
M. H. Bennett
S. D. Benoliel
E. R. Berry
Geo. M. Berry
W. Blum
C. J. Brockman
J. Rowland Brown
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W. G. Harvey
Carl Hering
R. P. Heuer
Alcan Hirsch
Carl D. Hocker
Frank Hodson
Geo. B. Hogaboom
B. S. Hopkins
Henry Howard
W. L. Howe
Geo. F. Hughes
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R. W. Milnes
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A. W. Whitaker
R. H. White
O. G. Willey
H. M. Williams
Dudley Willcox
H. A. Winne
F. L. Wolf
F. Zimmerman

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C. B. Bellis, New York City
R. N. Blakeslee, Philadelphia, Pa.
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J. B. Remer, Elizabeth, N. J.
A. E. Rhoads, Detroit, Mich.
Mrs. Wm. J. Rich, Washington, D. C.
Wm. Romanoff, Mansfield, Ohio
Mrs. G. A. Roush, Bethlehem, Pa.
M. D. Sarbey, Cleveland, Ohio
Chas. W. Saxe, Worcester, Mass.
Willard Scott, N. Bancroft, Me.
R. Sibley, Philadelphia, Pa.
C. A. Smith, Bethlehem, Pa.
Edwin Smith, Jr., Orange, N. J.
Walter S. South, Elizabeth, N. J.
Mrs. H. N. Spicer, New York City
Mrs. C. J. Thatcher, New York City
C. T. Thomas, Washington, D. C.
Mrs. L. S. Thurston, Schenectady, N. Y.
Van Winkle Todd, Milburn, N. Y.
R. J. Traill, Ottawa, Canada
R. U. Townsend, Riverton, N. J.
L. J. Trostell, Joliet, Ill.
Mrs. F. M. Turner, New York City
Alois Von Isakovics, Monticello, N. Y.
Mrs. Frank J. Vosburgh, New Rochelle, N. Y.
Clifford S. Ware, Philadelphia, Pa.
E. H. Watkins, Philadelphia, Pa.
W. M. Weigel, Washington, D. C.
J. F. White, Altoona, Pa.
A. M. Wightman, North East, Pa.
G. D. Williams, Worchester, Mass.
M. A. Williamson, Philadelphia, Pa.
T. A. Wilson, Palmerton, Pa.
W. C. Withan, Pittsburgh, Pa.
T. A. Wright, New York City
F. K. Ziegler, Harrison, N. J.

The Presidential Address presented at the Forty-fifth General Meeting of the American Electrochemical Society, in Philadelphia, Pa., April 25, 1924.

THE SERVICE RENDERED BY TECHNICAL SOCIETIES

By A. T. Hinckley.[1]

Since the very beginnings of organized society, thinking men have been questioning the utility of its various institutions. Today there arises the question, "Why do technical societies exist?" "What service do they render?" A new technique has come into the world, the technique of service. We all know what service means in business, but it has come to have a broader significance, that of putting the originality and inventiveness of the few to work for the good of the many.

Technical societies are in a particularly advantageous position to serve, standing as they do between pure science and industry. They extend one hand, as it were, to theory, and the other to practice. Their function may be best described as interpretive. Service is rendered to three distinct groups: To the science or art involved, to the general public, and lastly to the individual and his business affiliations. Let us examine each of these groups as to the service required and the service rendered.

Rendering service is an art. There is beauty in the service rendered by one individual to another, but how much more beautiful it is when a society, an aggregation of individuals, renders service to its science, each individual to the whole.

It is interesting to follow, through the eyes of the technical societies, the progress of science in its many relations. In its beginning science was a cloistered thing which was sufficient unto itself and did little to increase human happiness. It was a static phenomenon, a mere accumulation of observations and deduced facts. That first great Italian technical society gave life to science and started the movement which made of science the great dynamic force it is today. Just as the test of a sound education

[1] Chemist, National Carbon Co., Niagara Falls, N. Y.

lies less in our knowledge than in what use we make of it, so the criterion of advance in science is whether human life has been made more worth the living.

Technical societies have been called the "Salesmen of Science." At first glance it seems unthinkable that science should require salesmen. When one considers, however, the diversity of the field covered by even one small branch of science and the differences both of time and space which separate it from its dependent industries, the service rendered by the "Salesmen of Science," the technical societies, becomes apparent.

Science itself is served by industry through the technical societies. To science is given the task of explaining our life and environment. Science, therefore, never quite catches up with life. The observations from the manifold points of view of industry open up a new vista to science. But for science, such bypaths might never be explored; but for industry they might never have been opened.

The technical press serves in a similar way to connect science and industry, but since the contact is less direct, much of inspirational quality is lost in transmission. Direct discussion, which is impossible through the press, is conveniently arranged by the technical societies. It is perhaps by fostering this particular function that the technical societies may serve best.

The general public is served by technical societies in two ways, through the broadening of point of view of the members on technical subjects of public interest and to a lesser extent through furnishing of technical information to government agencies.

A technical training, on account of its highly specialized character, will not of itself fit a man to perform intelligently his duties as a citizen. It must always be remembered that education is more than the learning of a profession, it is the development of the mind. Technical societies supplement such specialized training with the broadening influence of discussion of varied subjects from many and varied points of view.

It is not the function of technical societies to participate as such in governmental activities. The political agencies already in existence are capable of conveying to our legislative bodies the consensus of public opinion. What is needed is a better

informed and more actively interested public. It is the duty of technical societies to discuss at their meetings such matters of public interest as fall within their respective fields. The broad, yet detailed, pictures thus presented are carried by each member to his own community, and it becomes his duty as a citizen to pass these pictures on to his associates.

Our Secretary of Commerce, Herbert Hoover, who is himself an engineer, sounded the keynote of the situation when he stated that "we are facing a time in the development of our civilization when we must find some sort of a bridge between the extreme individualism of the last century and the possible inroads of those forces that would extinguish that individualism entirely." I believe that bridge exists in ourselves and our present institutions. The growth of mutual confidence between technical societies has already led to the pooling of knowledge and ability for public service. This knowledge and ability can only become truly effective when we as citizens will that it be so. The technical societies can render a real service here by so arranging for the discussion of technical subjects of live public interest that their members go to their homes resolved to use their citizenship to make such knowledge and ability active for the public good.

When considering what the individual member gets out of the technical societies, we must remember that the unselfishness bred through giving is as true of ideas as of other forms of wealth. In this case the individual has a great advantage, for as he gives of his ideas to the many, so the gift returns multiplied.

If, perchance, he is unable to attend the meetings of his society, he may still participate through the technical and scientific papers and communicated discussions. These form the background of fundamental knowledge, which is requisite to progress in the art. The absent member loses the inspiration which can only be derived from conversation with others interested in his or allied work. Only through direct contact can he gain a thorough understanding of the personality of the author. Such an understanding is necessary to an appreciation of his point of view. It is this development of mutual understanding of point of view which is most essential, as it is the foundation for the development of mutual confidence which is the basis of progress.

Just as mutual confidence may be established between individuals, so it may be developed between group interests. This belief has led in the past few years to an increasing number of group discussions. It is perhaps too soon to make an estimate of the value of these discussions. They are being tried, however, in many fields and success is indicated already by the growing recognition of the unity of many problems which were once considered separate. By fostering group discussions, technical societies will, I believe, render one of the greatest services within their scope.

There is still need for the specialized technical society, as there is need for the specialist in any profession. Its transactions contain the detailed knowledge of the art. In the group discussions, light from many sources is turned on the problem of the hour. The first result is a clearer view than is possible from one angle alone. This growth of group discussion is a natural result of the growth of mutual confidence. Each group, as it knows the other better, reveals more and more of the so-called "secrets of the trade." As a matter of fact, these "secrets" are usually as well known outside the trade as they are within its confines. You can all recall many cases where such "secrets," cherished in an art for years, when revealed proved worthless, while observations passed by as insignificant took on new meaning when viewed from a new angle.

No society need fear losing its prestige by participation in a group discussion fostered by another society. If a new idea be born, the glory will be enough for all.

When the first great industrial research organizations were built up similar fears were expressed as to the possible loss of individuality of their members. Time has shown that not only were these fears groundless, but that in addition there has grown up a spirit of teamwork in research. This new spirit is not only an added honor to each member, but gives to the whole a capacity for service which exceeds the sum of their abilities as individuals.

Such a spirit will, I believe, develop in technical societies through group discussions. At present there is an unnecessary duplication of effort. In order to follow the progress of an art of even limited scope, one must belong to several societies. Under

this arrangement no one society can give to its programmes the completeness and continuity that is desirable. As mutual confidence develops between societies, a plan for co-operation will undoubtedly be devised. Then technical societies will be able to render the full rounded service that each member has the right to expect.

Being devoted to the correlation of theory and practice, technical societies form a natural bridge for linking the educational institutions to industry. The graduate, looking for a suitable place to start in industry, turns to the technical societies for a more detailed picture than he could get at college. He looks to their conventions as places where he may come to know the leaders in that industry he hopes to enter. By arranging for one or more periods of informal discussions at conventions, this service may be greatly enhanced. The differences between the every-day problems of industry and the theory of the text book are brought out in vivid contrast. These differences rise as a challenge to his imagination and creative effort. The possibilities of this transition were expressed most forcefully by Dr. Chas. P. Steinmetz: "Perhaps the difference between what he learned at school and what he finds in the world may teach him to think. That is the greatest thing that can happen to a man."

So technical societies bring to science the point of view of industry, to the state more interested and intelligent citizens and to the individual those new contacts and new vistas which "teach him to think."

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 24, 1924, President A. T. Hinckley in the Chair.

THE PRESENT STATUS OF APPLIED ORGANIC ELECTROCHEMISTRY.[1]

By Charles J. Thatcher.[2]

In connection with this symposium on organic electrochemistry it seemed well to ascertain to what extent electrochemical methods are being used, commercially, in the preparation of organic compounds. To this end, a committee of members of the Society, consisting of Messrs. Alexander Lowy, E. R. Weidlein and H. C. P. Weber, was appointed a year ago. Letters were sent out by the Society to about sixty manufacturers in this country, asking them to state whether they were manufacturing organic substances by electrochemical processes or preparing to do so, and to give any other information which they cared to reveal.

The letters were sent to those manufacturers who would most likely be interested in the applications of organic electrochemical methods, and to a few individuals who would be most apt to know of such applications. Through the United States Department of Commerce an inquiry was also forwarded to Dr. Fred. E. Breithut, its chemical representative in Germany, to ascertain, if possible, the status of the industry in Europe. An independent inquiry as to what was being done in Switzerland was also made.

Twelve replies have been received to these inquiries. Six of these replies indicated that investigations were being made, or that the manufacturers were at least interested in the commercial application of electrochemical methods in the preparation of organic compounds. Only one reply told of actual commercial

[1] Manuscript received March 27, 1924.

[2] Chem. Engr., New York City.

production of such compounds in this country at the present time. This will be referred to later, together with reference to another commercial application with which we were already familiar.

No reply has been received from Dr. Breithut as yet; the Department of Commerce writes that he will probably be too busy, before his return to this country in June, to give the subject his attention. However, it was reported by the correspondent in Switzerland that benzidene is being manufactured commercially in that country by an electrochemical process, and that in Germany some of the larger chemical works are using electrochemical methods for the production of anthraquinone. Further details are not available.

In this country the application of electrochemical methods to the production of organic compounds seems to have been confined, principally, to the regeneration of spent chrome liquors resulting from the use of chromic acid mixtures in the oxidation of anthracene to anthraquinone, toluene to benzoic acid, and naphthalene to phthalic anhydride. At the present time, no phthalic anhydride is being manufactured here in this manner, so far as we can learn; but formerly, during the war, a company in Ohio made, we understand, about 400,000 pounds of phthalic anhydride, the spent chrome liquors resulting from this operation being regenerated electrolytically. The same company also made 15,000 pounds or so of benzoic acid and 5,000 to 6,000 pounds of anthraquinone, also accompanied by the electrolytic regeneration of spent chrome liquors. [All of these operations were discontinued several years ago, but not because the operations were not practical or economical, it is said.]

At the present time a manufacturing concern in New England is making, we are informed, 1,200 to 1,500 pounds of benzoic acid per week by bichromate oxidation, in which electrolytic methods are used to regenerate the spent liquor. This process has been in operation for several years with short interruptions. The advantage of the method is claimed to be that benzoic acid, or its sodium salt, can be produced which is free from chlorine or nitrobenzoic acid, both of which give an objectionable taste or odor to benzoic acid or benzoates when used as preservatives. It

would appear, from the length of time during which the operations have been continued, that the method in use is commercially successful.

Another concern in New York State has been using Niagara Falls power for about three years in the regeneration of spent chrome liquors, resulting from bichromate oxidation of anthracene to anthraquinone. The same lot of spent chrome liquors has been regenerated many hundreds of times, the only losses being those due to leakage or to losses of such chromium compounds as could not be completely washed out of the anthraquinone. This company claims, upon the basis of its extensive experience, that the saving effected by use of the electrolytic regeneration process is about 26 cents per pound of anthraquinone produced.

It is reported that this company has had no difficulties since the start with those of its operations which are of an electrolytic nature, and that the cells and diaphragms have proven to be durable in daily use extending over a period of many months. Many tons of anthraquinone have been produced by this company and enlargement of its plant is contemplated.

The only commercial operations known to us, involving the production of an organic compound directly in an electrolytic cell, were those in which, during the war, the writer made several tons of paramidophenol sulphate for use as a photographic developer. This production, and other commercial electrochemical productions of various organic compounds said to have been carried on in Germany and Switzerland, are referred to in a paper presented at the fall meeting of this Society in 1919.[3]

The restriction of organic electrochemical operations, principally, to the regeneration of spent chrome liquors, is ascribable to the ease of such operations now that suitable cells and diaphragms are available. However, with such equipment, there is no inherent difficulty in the direct production of organic compounds, commercially, by electrochemical methods and in the cells themselves. The fact that such methods have not been used commercially for that purpose is attributable only to lack of interest and foresight, on

[3] Trans. Am. Electrochem. Soc., 36, 337-348 (1919).

the part of manufacturers, sufficient to work out practical details necessary for the industrial application of many known and promising organic electrochemical processes. Some manufacturers, however, are beginning to awaken to the possibilities, and there is every reason to believe that impetus will be given to the development of this industry in the near future by investigations now under way.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 24, 1924, Dr. C. J. Thatcher in the Chair.

THE ELECTROLYTIC PREPARATION OF SALICYLIC ALDEHYDE FROM SALICYLIC ACID.[1]

By Kendall S. Tesh with Alexander Lowy.[2]

Abstract.

Salicylic aldehyde is prepared electrolytically by the reduction of salicylic acid (sodium salt) to the aldehyde. The ordinary type of diaphragm cell is used with a mercury cathode, using boric acid and sodium sulfate as catholyte. A current density of 6 amp. per sq. dm. is used, and the temperature is kept between 15° and 18° by means of a freezing mixture. The aldehyde is fixed as soon as formed by means of sodium bisulfite, and is recovered by means of acid hydrolysis and steam distillation. Up to the present stage of the process the best yield obtainable is 55 per cent.

The purpose of this research was to study the experimental details for the preparation of salicylic aldehyde by the reduction of salicylic acid (sodium salt) electrolytically.

In 1906 Dr. Hugo Weil patented a process[3] for the reduction of salicylic acid to salicylic aldehyde electrolytically. However, a number of important experimental details were omitted and no yields were stated. Two years later an article by Carl Mettler[4] appeared on the electrolytic reduction of salicylic acid (sodium salt) to salicylic aldehyde which was identical with the patent of Weil.

Several important details are lacking in the publication. The article claims from 30 to 50 per cent yield of salicylic aldehyde,

[1] Manuscript received February 12, 1924.

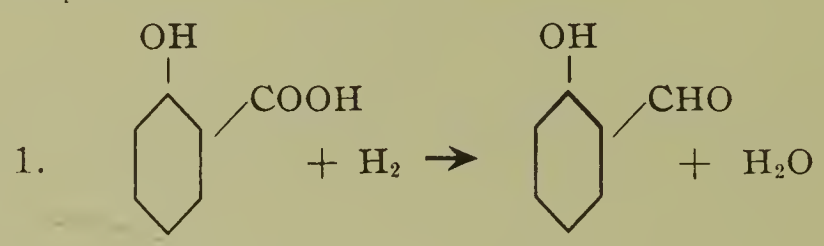
[2] Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

[3] D. R. P., 196,239 (1906).

[4] Ber., **41**, 4,148 (1908).

but the best yield the writers could obtain by following the details given was 20 per cent. It was for the purpose of increasing the yield and working out the details of the process that this research was undertaken.

When salicylic acid is reduced with the reducing agents commonly employed in the laboratory, the chief product is salicyl alcohol.[5] This salicyl alcohol on treatment with acids is converted into a resinous product forming "saliretin." The reduction, however, should take place in two stages, going first to the aldehyde and then to the alcohol, as follows:



Since the second step in the reduction seems to take place more readily than the first, it is evident that something should be put into the solution, which will remove the aldehyde produced as fast as it is formed, either by extraction or combination, thus protecting it from further reduction to the alcohol.

A number of different methods were tried to accomplish this result. First, removal by steam distillation as fast as formed; second, extraction with benzene; and third, combination with *p*-toluidine, *β*-naphthylamine and sodium bisulfite. Up to the present point in the research, combination with sodium bisulfite seems to give the best results.

EXPERIMENTAL PART.

The usual diaphragm type of electrolytic cell is used in all of the experiments except those at a boiling temperature. (Experiment No. 10, Table I.) The cell is immersed in a cooling mixture or cold water to maintain the desired temperature. A mechanical stirrer is used in all experiments. Unless otherwise stated, the

[5] Ber., **39**, 2,933 (1906).

mercury layer is not stirred with the mechanical stirrer. In all cases a platinum spiral anode is used. A typical experiment is as follows: (Experiment No. 15, Table I).

The bottom of a 600 cc. low form beaker is covered to a depth of 1 cm. with mercury, which serves as the cathode. This gives an area of 50 sq. cm. Two cylindrical, porous cups (8 x 2 cm.) are suspended from the sides of the beaker so that the bottoms of the cups are about 2 cm. from the surface of the mercury. These hold the anodes which consist of two coils of platinum wire. The anolyte is 10 per cent sodium sulfate solution. The cathode mercury layer is connected to the source of current by means of a platinum wire encased in glass tubing.

Into the cell is then placed a solution of 15 g. sodium sulfate, 15. g. boric acid and 14 g. of salicylic acid (0.1 mole), just neutralized with the calculated amount of sodium hydroxide. The solution is then diluted to 175 cc. All the boric acid does not dissolve in this quantity of solution, but is kept in suspension by means of rapid mechanical stirring. The cell is placed in a cooling mixture, and when the temperature reaches 15° to 18° the current is turned on. A temperature of 15° to 18° is maintained throughout the experiment. A current of 3 amp. (6 amp. per sq. dm.) is then passed through the solution for a period of 1 hr. 55 min., which is slightly more than the calculated amount (5.4 amp.-hr.) necessary to reduce the salicylic acid to salicylic aldehyde. During the electrolysis 20 g. sodium bisulfite are added at the rate of about 1.5 g. every 10 min. It has been found best not to begin the addition of the sodium bisulfite until the electrolysis has been started about 5 min., since the bisulfite is reduced to sulfur when added too soon, or too rapidly thereafter.

At the conclusion of the electrolysis the porous cups are removed, washed with distilled water, and the white precipitate, which usually collects on the outside, scraped off and returned to the solution. This white precipitate consists chiefly of boric and salicylic acids. The stirring is continued for 30 min. after the current is shut off in order to make use of the sodium amalgam, which is built up during the electrolysis. The solution is then decanted from the mercury, which is washed several times with 50 cc. portions of distilled water. Then 20 cc. concentrated

TABLE I.

Details of the Electrolytic Preparation of Salicylic Aldehyde.

In all the experiments, the amount of salicylic acid specified was added as sodium salt.

Expt. No.	Purpose	Catholyte	Anolyte	Cathode and size	Amp.	V.	Time in Amp.-hr.	Temp. °C.	Per cent Yield of Salicylic Aldehyde	See Notes on p. 44
1	According to Mettler Specifications. (Ber. **41,** 4148)	15 g. Na_2SO_4, 15 g. H_3BO_3 14 g. Sal. acid in 250 cc. water with 100 cc. benzene	10% Na_2SO_4	Hg 78 sq. cm.	1.8	14	7.2	30-33	15	(1)
2	Same as 1	Same as 1	10% Na_2SO_4	Same as 1	1.5-2.0	12	9	20	20	(1)
3	Effect of *p*-toluidine as condensing agent. (Added as solid.)	15 g. Na_2SO_4, 15 g. H_3BO_3 14 g. Sal. acid in 175 cc. water.	10% Na_2SO_4	Hg 50 sq. cm.	3	16-18	6	30	15	(2)
4	Same as 3, filtering cond. product before hydrolysis.	Same as 3	10% Na_2SO_4	Same as 3	2	14-18	7	30	30	(3)
5	Same as 3, *p*-toluidine first dissolved in 50 cc. alcohol.	Same as 3	10% Na_2SO_4	Same as 3	2	18-20	7	30	20	(4)
6	Same as 3, using higher concentration of alcohol.	15. g. Na_2SO_4, 15 g. H_3BO_3 14 g. Sal. acid in 90 cc. alcohol and 85 cc. water.	10% Na_2SO_4	Same as 3	1	14-18	6	30	8	(5)

7	Effect of β-naphthylamine added as cond. agent. (Added as solid.)	Same as 3	10% Na_2SO_4	Same as 3	2	14-16	8	30	2	(6)
8	Without boric acid with addition of $NaHSO_3$	Same as 3, in 250 cc. water and with 20 g. $NaHSO_3$ added gradually.	10% Na_2SO_4	Same as 1	1.5	10	8	30	trace	(7)
9	No diaphragm.	Same as 3, with the addition of 20 g. $NaHSO_3$	10% Na_2SO_4	Same as 3	2	10	5	30	none	(8)
10	Steam distillation of aldehyde as formed.	Same as 3, in 500 cc. water.	10% Na_2SO_4	Same as 3	1.5-2.0	16-18	6	100	none	(9)
11	Effect of $NaHSO_3$	Same as 3, with the addition of 20 g. $NaHSO_3$	10% Na_2SO_4	Same as 3	3	10	6.75	30	30	(10)
12	Effect of temperature with sodium bisulfite.	Same as 11	10% Na_2SO_4	Same as 1	2	10	6.5	45	trace	(11)
13	Same as 12	Same as 11	10% Na_2SO_4	Same as 1	2	10	8	36	trace	(12)
14	Same as 12	Same as 11	10% Na_2SO_4	Same as 3	2	10	8	30	30	(13)
15	Same as 12	Same as 11	10% Na_2SO_4	Same as 3	3	14	5.4	15-18	55	(14)
16	Same as 12	Same as 11	10% Na_2SO_4	Same as 3	3	14-18	5.4	5-7	5	(15)
17	Effect of current density at 30° C.	Same as 11	10% Na_2SO_4	Same as 3	1	8	6	30	trace	(16)

TABLE I—Continued.

No. Expt.	Purpose	Catholyte	Anolyte	Cathode and size	Amp.	V.	Time in Amp.-hr.	Temp. °C.	Per cent Yield of Salicylic Aldehyde	See Notes on p. 44
18	Same as 17	Same as 11	10% Na_2SO_4	Same as 3	2	10	8	30	30	(17)
19	Same as 17	Same as 11	10% Na_2SO_4	Same as 3	3	10	6.75	30	30	(17)
20	Same as 17	Same as 11	10% Na_2SO_4	Same as 3	4	14-18	6	30	50	(18)
21	Effect of current density at 15°-18°	Same as 11	10% Na_2SO_4	Same as 3	1.5-1.6	14	5.4	15-18	10	(19)
22	Same as 21	Same as 11	10% Na_2SO_4	Same as 3	2.5	16-18	5.4	15-18	12	(20)
23	Same as 21	Same as 11	10% Na_2SO_4	Same as 3	3	14	5.4	15-18	55	(14)
24	Same as 21	Same as 11	10% Na_2SO_4	Same as 3	4	16-18	5.4	15-18	40	(18)
25	Same as 21	Same as 11	10% Na_2SO_4	Same as 3	5.4	18-25	5.4	18	40	(18)
26	Effect of intermittent electrolysis	Same as 11	10% Na_2SO_4	Same as 3	3	16-18	6	15-18	50	(21)
27	Effect of time.	Same as 11	10% Na_2SO_4	Same as 3	3	14	18	15-18	47	(22)

28	Effect of stirring mercury.	Same as 11	10% Na_2SO_4	Same as 3	3	14	5.4	15-18	10	(23)
29	Effect of conc. of salicylic acid.	Same as 3, in 250 cc. water with 20 g. $NaHSO_3$ added.	10% Na_2SO_4	Same as 1	2	14	10	30	17	(24)
30	Same as 29	15 g. Na_2SO_4, 15 g. H_3BO_3 28 g. Sal. acid, in 250 cc. water with 20 g. $NaHSO_3$	10% Na_2SO_4	Same as 1	2	10	13	30	25	(25)
31	Same as 29	Same as 30, in 175 cc. water.	10% Na_2SO_4	Same as 3	3	16-18	5.4	15-18	47.5	(26)
32	Effect of Cu-Hg cathode	Same as 11 (double quantities).	10% Na_2SO_4	Cu-Hg 265 sq. cm.	2.5	12-14	13	30	trace	(27)
33	Effect of Pb cathode	Same as 29	10% Na_2SO_4	Pb 80 sq. cm.	2	12-14	8	30	none	(28)
34	Sodium acetate for sodium sulfate.	Same as 11, with 20 g. $NaC_2H_3O_2$ in place of sodium sulfate.	10% $NaC_2H_3O_2$	Same as 1	2.3-2.4	15	7	30	trace	(29)
35	Sodium chloride for sodium sulfate.	Same as 11, with 15 g. NaCl for sodium sulfate.	10% NaCl	Same as 3	2	10-14	6	30	5	(30)
36	Calcium chloride in place of sodium sulfate.	Same as 11, with 15 g. $CaCl_2$ instead of Na_2SO_4	10% $CaCl_2$	Same as 3	3	18	7	30	1	(10)
37	Potassium sulfate in place of sodium sulfate.	Same as 11, using 15 g. K_2SO_4 and potassium salt of salicylic acid.	10% K_2SO_4	Same as 3	3	14-16	5.4	15-18	20	(31)
38	Effect of larger quantity.	Same as 11, using four times all quantities.	10% Na_2SO_4	Hg 113 sq. cm.	6.5	18	21.6	15-18	31.5	(19)

TABLE I—Continued.

Details of the Electrolytic Preparation of Salicylic Aldehyde.

The numbers preceding the following notes refer to the corresponding figures in the last column of the Table.

1. Resin formed. No salicylic acid recovered.
2. Hydrolyzed with 20 cc. H_2SO_4. Considerable amount of resin formed.
3. Condensing product filtered off before hydrolysis. Less resin formed.
4. Same as note 2 above. 8 g. resin formed.
5. Same as note 2 above. 11.5 g. resin formed.
6. Same as note 2 above. Much resin formed.
7. 10 g. salicylic acid recovered. Some sulfur formed.
8. White precipitate (salicylic and boric acids) separated out on anodes. Much SO_2 evolved.
9. Hydrogen was evolved, and much resin formed.
10. Resin formed and a very small amount of salicylic acid recovered.
11. 10 g. salicylic acid recovered.
12. 12 g. salicylic acid recovered.
13. Resin formed. No salicylic acid recovered.
14. Very small amount of resin formed.
15. 7 g. salicylic acid recovered. Most of material was precipitated from solution.
16. 11 g. salicylic acid recovered.
17. Resin formed. No acid recovered.
18. Small amount of resin. No salicylic acid recovered.
19. 7 g. salicylic acid recovered. Some resin.
20. 6 g. salicylic acid recovered. Some resin and some sulfur formed.
21. Electrolyzed 30 min.; off 10 min.; on 30; off 10; etc. A little resin. No acid recovered.
22. More resin than usual. No acid recovered.
23. 10 g. salicylic acid recovered. Sulfur formed.
24. Some sulfur formed. No acid recovered.
25. Resin formed and about 2.5 g. acid recovered.
26. Resin formed. 10 g. acid recovered.
27. A copper beaker amalgamated with mercury on the inside was used in this experiment. 18 g. salicylic acid recovered. Some resin.
28. 12 g. salicylic acid recovered.
29. 13 g. salicylic acid recovered.
30. 8 g. salicylic acid recovered.
31. 7 g. salicylic acid recovered. Small quantity of resin.

H_2SO_4 in 100 cc. of water are added to the solution and steam distilled.

The salicylic aldehyde distills over as a very pale yellow oil, heavier than water, and collects at the bottom of the receiver. The steam distillate is then extracted with ether, the extract treated with $NaHCO_3$ to neutralize any acid which distills over, then dried over Na_2SO_4 and distilled. The residual liquor after steam distillation always contains some resin (0.2-2.0 g.) It is filtered hot and allowed to cool, in order to recover any unused salicylic acid. In this experiment no salicylic acid is recovered.

Yield of salicylic aldehyde 6.7 g., 55 per cent. Current efficiency the same. The yield was calculated on the total amount of salicylic acid started with. Experiment No. 38 gives experimental data for four times the quantity of material used above.

The experiments listed in Table I were conducted under variable conditions for the preparation of salicylic aldehyde. The purpose of each experiment is given in column 2.

DISCUSSION OF RESULTS.

From the results in Table I it is found that the use of sodium bisulfite materially increases the yield of salicylic aldehyde. Further, that the lower temperatures (15° to 18°) favor the yield of salicylic aldehyde. At higher temperatures less salicylic aldehyde is produced and more of the resinous product. Up to a current density of 8 amp./sq. dm. the yield of salicylic aldehyde is increased. Intermittent electrolysis or stirring after electrolysis is necessary for good current efficiency since a sodium amalgam is built up during the electrolysis. Increasing the time of electrolysis seems to increase the quantity of resin formed. Increasing the concentration of salicylic acid (sodium salt) has little or no effect.

Further work is in progress to increase the yield of salicylic aldehyde.

DISCUSSION.

C. J. THATCHER[6]: In the commercial application of organic electrochemical methods low yields are partly due to the fact

[6] Chem. Engr. and Electrochemist, New York City.

that in addition to the *desired* electrochemical processes other reactions are apt to occur. This is particularly true where the desired end-product is soluble in the electrolyte. It is very difficult to get this end-product unless it is not subject to further oxidation or reduction. One way to overcome this, of course, is to remove the desired compound as fast as it is formed. Prof. Lowy and his co-workers tell us of one method whereby this may be accomplished.

One ideal way to catch the fleeting compound that we want is to dissolve it in an immiscible solvent. I note that Prof. Lowy tried the solution of aldehyde in benzene. What result did you obtain?

ALEX. LOWY: That was the patent indicated in Hugo Weil's work. Mettler's object was, that as soon as the aldehyde was formed it should be extracted in benzene, and for that reason he added a certain amount of benzene—I think something like 100 cc. to about 250 cc. Now we did that, as a matter of fact, we repeated it two or three times, and the maximum yield obtained according to Mettler's specification was 15 to 20 per cent. You can readily see that when you stir benzene into the solution there is still free aldehyde present, and of course this means that it would respond to further reduction to alcohol.

C. J. THATCHER: Did you try circulating it in and out during the electrolysis in order to keep the concentration of the aldehyde low?

ALEX. LOWY: We did not try that with benzene because the yields were low. They claimed from 30 to 50 per cent yield, and we tried at least six or eight experiments under different conditions according to their specifications, and the maximum yield we were able to obtain was about 20 per cent.

C. J. THATCHER: I know of one application in which the desired end product is being dissolved in an immiscible solvent, and flowed out so that its concentration is kept low and there is no chance of further oxidation.

ALEX. LOWY: With an overflow effect and a subsequent recovery of the solvent no doubt a better yield could be obtained.

H. C. P. WEBER[7]: I am interested in knowing something of the nature of the by-products. Was the inefficiency of the process of

[7] Research Engr., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

reduction due to the loss of hydrogen, or was it due to the further reduction of, say, alcohol?

ALEX. LOWY: There may have been a certain amount of hydrogen loss. On the other hand, if you will look on page 44 you will find that in only a few cases was salicylic acid recovered. During steam distillation a resin was formed. The composition of this resin is not known, but it is a fact that salicylic alcohol when treated with acid produces a resin known as "saliretin." There was a certain amount of resin produced in all the experiments. We found the one with sodium bisulfite gave the least amount of resin, which showed that the aldehyde was fixed. Besides this point, we wanted to be absolutely certain as to whether the sodium bisulfite was necessary to give us the yield, so we tried an analogous experiment with every other detail duplicated except the sodium bisulfite, and we found that only a trace of aldehyde was produced.

F. C. FRARY[8]: I notice there is only one experiment on the effect of stirring the mercury, and that seems to have had, as would be expected, the same effect as a lower current density, in that you reduced the concentration of the sodium amalgam at the surface. If you use constant current density and do not stir, it is going to be very difficult to maintain your sodium amalgam concentration correctly. It seems to me advisable, therefore, to try to increase the allowable current density by stirring the mercury. You could more accurately control the composition, and especially it would much facilitate cooling the solution. I should think that, on a larger scale, one of the principal problems would be to keep your temperature down. You can cool the solution so much more easily by cooling your mercury, and letting the mercury take the heat out of the water, than you can by introducing cooling coils.

ALEX. LOWY: Before any reduction takes place we must have a certain concentration of sodium amalgam built up. With stirring, the sodium amalgam decomposed too rapidly to give a good current efficiency. Regarding the temperature effect, you are correct.

C. J. BROCKMAN[9]: I wonder, since Dr. Lowy mentions the

[8] Director of Research, Aluminum Co. of America, New Kensington, Pa.
[9] Dept. of Chemistry, Univ. of Georgia, Athens, Ga.

formation of an amalgam, whether we are dealing strictly with an electrolytic reduction. The mercury cathode is the only one that works. Is this not good evidence that we are dealing with a chemical rather than with an electrolytic reaction. The cathodic overvoltage of these electrodes is high. In a reduction like this, where the reaction is to be stopped at an intermediate compound, a low cathodic overvoltage is very desirable. Would not a platinum cathode work as well or better?

ALEX. LOWY: Whether this is an electrochemical or purely a chemical process, I would say that the formation of the sodium amalgam is an electrolytic process, and the subsequent reduction is probably a purely chemical one. It is comparatively easy to build up a sodium amalgam electrolytically, which in turn is to be used for reduction.

C. J. THATCHER: Did you try platinum or any other metal?

ALEX. LOWY: We have not tried platinum, because the hydrogen overvoltage of platinum is very low, but we have tried copper and a few others which are intermediate. Some of these *e. g.,* copper, do not work. We tried lead, lead being lower than mercury. We also tried other amalgams and electrolytes like potassium amalgam and sodium acetate. We get more hydrogen loss and less yield with potassium than with sodium amalgam. We have also tried calcium amalgam.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 24, 1924, Dr. C. J. Thatcher in the Chair.

THE ELECTROLYTIC REDUCTION OF BETA-ANTHRAQUINONE SULFONIC ACID.[1]

By Alfred R. Ebberts with Alexander Lowy.[2]

Abstract.

A preliminary study was made on the electrolytic reduction of β-anthraquinone sulfonic acid. In sulfuric acid solution the golden yellow color of β-anthraquinone sulfonic acid is converted to an olive-green "vat" (β-anthraquinol sulfonic acid), which on aeration reverts to the original substance. On further reduction, the olive-green "vat" is converted to a yellow solution (probably β-anthrone sulfonic acid), which on aeration does not revert to the original substance. Reduction of sodium β-anthraquinone sulfonate produces the typical red "vat," which on aeration reverts to the original salt.

A theoretical consideration of the reduction of anthraquinone[3] reveals the reaction taking place in the steps as shown on following page.

This reduction can be actually followed experimentally under variable conditions.[4] The first product is a beautiful deep carmine "vat," shown by Grandmougin[5] to be anthraquinol, although it does not fluoresce as would be expected of any compound having the anthracene bridge, which fact led many investigators to favor the hydroxyanthrone structure. Anthraquinol is undoubtedly the first product in acid solution as Liebermann[6] carried out the

[1] Manuscript received February 15, 1924.

[2] Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

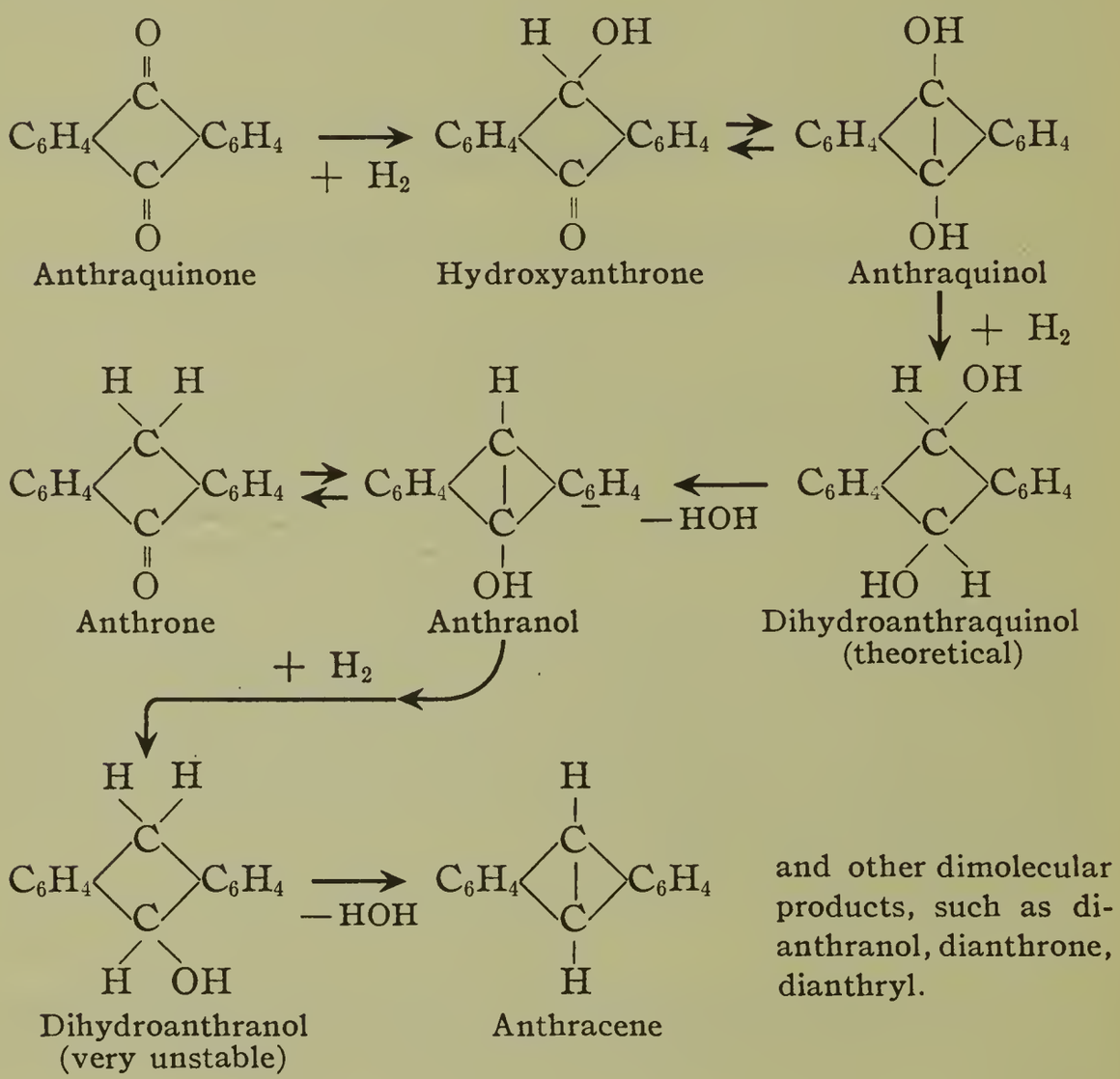
[3] Richter-D'Albe, Organic Chemistry, II, 710 (1922).

[4] Barnett, Anthracene and Anthraquinone, p. 80-85 (1921).

[5] Barnett, Anthracene and Antharquinone, p. 83 (1921).

[6] Ber. 21, 436 (1888).

reduction, with acetic anhydride and zinc in the presence of sodium acetate, obtaining the diacetyl derivative of anthraquinol directly.



and other dimolecular products, such as dianthranol, dianthrone, dianthryl.

The sodium salt of β-anthraquinonesulfonic acid has also been reduced by Liebermann[7] using red phosphorus and hydriodic acid of varying strength. He was able to obtain the corresponding sodium anthracenesulfonate, the meso-dihydroanthracene sodium sulfonate, and finally meso-dihydroanthracene itself. He says nothing of the products intermediate between the anthraquinonesulfonic acid and anthracenesulfonic acid (sodium salts), corresponding to the above-shown products of the reduction of anthraquinone. It was the purpose of the present investigation to study the formation of the intermediate reduction products of β-anthraquinone sulfonic acid by electrolytic means. The fact that the

[7] Ann., 212, 48 (1882); Ber., 12, 589 (1879).

sulfonic acids and their salts are soluble to more or less extent in aqueous media is a decided advantage for this type of experimental work.

EXPERIMENTAL PART.

A stock solution of β-anthraquinonesulfonic acid was made by sulfonating Kahlbaum's chemically pure anthraquinone. The sulfonation liquor was poured into water, and the unchanged anthraquinone filtered off, washed acid free, dried and weighed. The filtrate was then made up to such volume that 100 cc. of the solution represented one gram of anthraquinone unrecovered. The solution had a golden yellow color.

Five hundred cc. of the stock solution was heated to 95° and 20 g. of NaCl added. The resultant sodium salt was filtered off, washed acid free, dried and converted into the sulfonchloride as follows. One part of the sodium salt, two parts of PCl_5 and five parts of $POCl_3$ were placed in a 100 cc. round-bottomed flask fitted with a reflux air-condenser carrying a $CaCl_2$ drying tube. The flask was placed in an oil bath, which was heated to 120° over a period of one hour, and kept at that temperature for three hours. The mixture was then poured into finely cracked ice and the solid material separating in the ice-water was filtered off, washed acid free with water, dried and recrystallized from benzene. Two recrystallizations gave a light yellow crystalline material melting at 193°, as given in Beilstein[8] for β-anthraquinonesulfonchloride. The 5.74 g. obtained is equivalent to a 78 per cent. yield.

Two hundred and fifty cc. of the stock solution, as catholyte, was reduced electrolytically, using a platinum foil cathode of one square decimeter area at a temperature of 70°. The anode was also of platinum foil, of 0.05 sq. dm. area, and enclosed in an unglazed porcelain cup. The anolyte was 20 per cent sulfuric acid. Mechanical stirring was used. These details of the cell were unchanged throughout this investigation. A current of one ampere was supplied to the cell, necessitating at first a pressure of 14 v., which gradually decreased to 4 v. The original golden yellow color of the solution gradually changed, becoming a beautiful deep olive-green in a half hour. A portion was removed

[8] Beilstein, III, p. 415 (1897).

and air was bubbled through it, dissipating the dark green color and restoring the golden yellow of the original solution. This ease of re-oxidation is characteristic of the "vats," and was taken to indicate that this green color was due to β-anthraquinolsulfonic acid. When some of the deep green solution was made alkaline with sodium carbonate, a deep carmine red color was produced resembling alkali-reduced anthraquinone. The air re-oxidized portion of the electrolytic solution was subjected to salting out and the sulfonchloride made from the sodium salt as described above. This also melted at 193° after one recrystallization from benzene. Continuation of the reduction destroyed the green color, the solution turning yellow.

The purpose of the following experiment was to convert the β-anthraquinonesulfonic acid to β-anthracenesulfonic acid. Five hundred cc. of the stock solution was reduced in the cell (details above) using a current of 1.5 amp. for 45 min.; then a current of 1 amp. until a total of 4.07 amp. hr. had been supplied (theoretical to reduce to anthracenesulfonic acid, 3.87 amp. hr.). The original yellow color was again converted to green, and the green, in turn to yellow on further reduction. At this stage of the experiment the solution was divided into two parts. To one part 40 g. of NaCl was added, the increased amount being necessary to cause precipitation. On filtering, it was found necessary to use saturated brine for washing to avoid loss. The material was dried and an attempt made to make a sulfonchloride according to the above described conditions. No definite crystalline product resembling β-anthracenesulfonchloride could be isolated. The other portion of the electrolyte was replaced in the cell and oxidized, using a current of 0.5 amp., which gradually increased to 1 amp. as the resistance of the cell decreased. A total of 4.1 amp. hr. was supplied. 20 g. of NaCl was added, the sodium salt precipitated was filtered off, washed, dried and made into the sulfonchloride as above. The resultant material, after two recrystallizations from benzene, melted at 193°. The results of this experiment indicate that the β-anthraquinonesulfonic acid was reduced further than the β-anthraquinolsulfonic acid stage (golden yellow color to olive green, then to yellow). This reduced product was then oxidized electrolytically back to anthraquinonesulfonic acid.

The yellow solution obtained on reduction through the green stage cannot be re-oxidized by bubbling air through it, therefore it can hardly be a "vat." As it does not give the anthracene-sulfonchloride described by Werner Heffter[9], it is not anthracene-sulfonic acid. The only plausible explanation is that it is a compound intermediate between the "vat" and anthracenesulfonic acid, either anthranol or anthrone sulfonic acid, or a mixture of intermediate products. It is probably the anthronesulfonic acid since the anthranolsulfonic acid should be fluorescent.[10] If the reduced solution is made alkaline and heated for two or three hours at eighty degrees it takes on a deep red color which it loses on cooling and standing, more readily if acidified. This is a characteristic change for the anthrone and anthranol type of tautomerism.[10]

To furnish material for two more attempts at making the β-anthracenesulfonchloride, 500 cc. of the stock solution was reduced as in the previous experiment. Since Heffter did not furnish exact details for this preparation, the following experiments were performed. The proportions of PCl_5 and $POCl_3$ were not varied, but only the time and temperature of digestion. One was heated to 100° for 1 hr. the other to 50° for 2 hr. The separations and recrystallizations were carried through as before. No definite crystalline product was isolated.

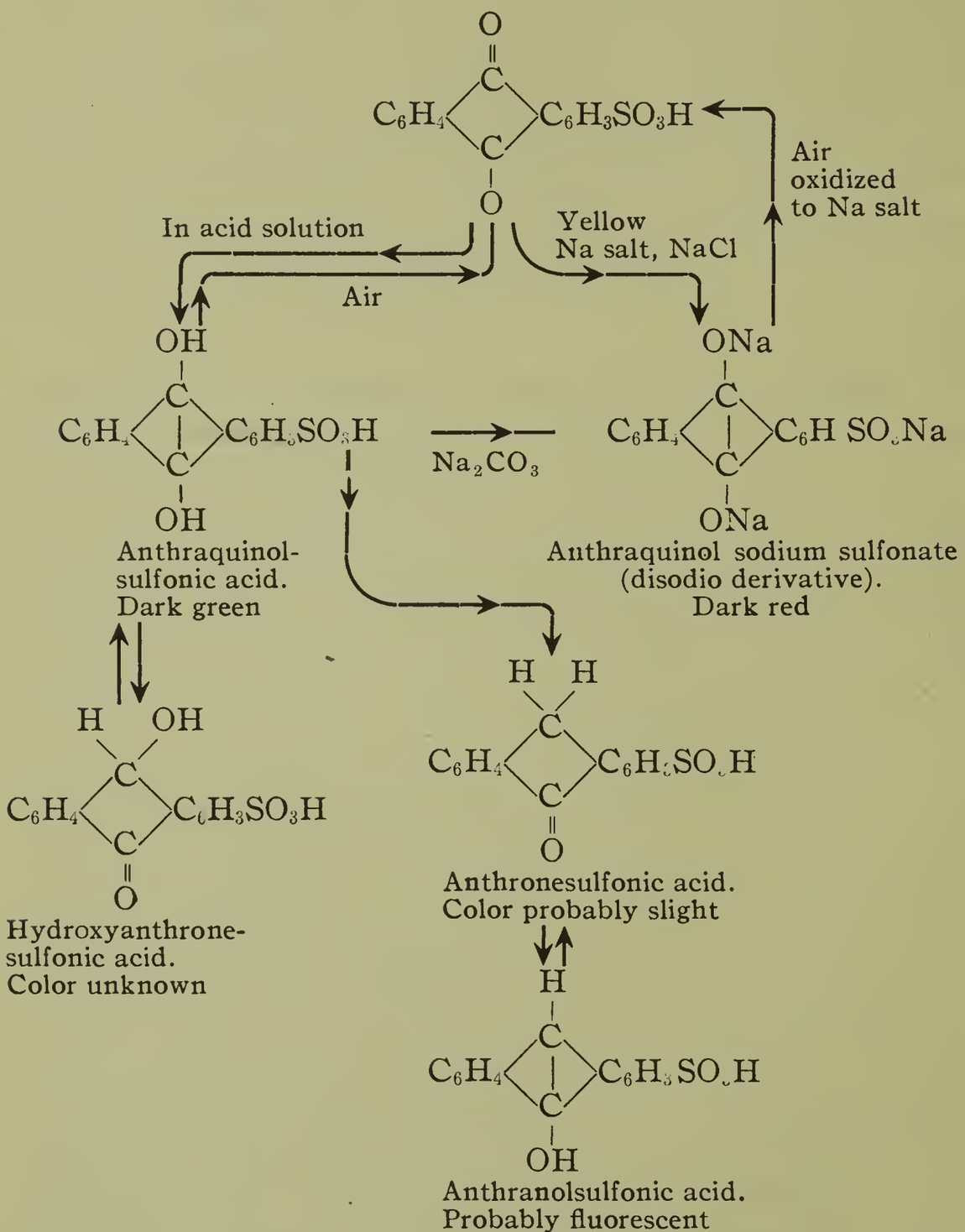
Two hundred and fifty cc. of the stock solution was treated with 20 g. of NaCl at 95° and the sodium salt filtered off and washed with brine. It was then suspended in 250 cc. of water and electrolytically reduced, using an iron cathode of 0.5 sq. dm. area and a current of 1 amp. The platinum anode was enclosed as before in a porous cup. The suspended particles gradually dissolved, and the characteristic dark red solution of the "vat" was obtained. Apparently the reduction did not go beyond this stage, although more than twice the theoretical amount of current was passed and a temperature of 85° maintained. After 4.5 amp. hr. had been supplied the solution was aerated. The original color and precipitate were restored by this process. The sodium salt was filtered off, dried and made into the sulfonchloride, which melted at 193.5° after one recrystallization from benzene.

[9] Ber., 28, 2262 (1895).

[10] Barnett, Anthracene and Anthraquinone, p. 118 *et seq.* (1921).

CONCLUSION.

1. Electrolytic reduction of β-anthraquinonesulfonic acid produces an olive green "vat" in acid solution which on aeration reverts to the original substance.



2. On further reduction the "vat" is converted into a yellowish solution, which on aeration does not revert to the original β-anthraquinonesulfonic acid.

3. Reduction of β-anthraquinone sodium sulfonate electrolytically produces the dark red "vat", which on aeration reverts to the original salt.

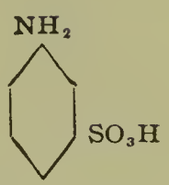
4. From the foregoing it is concluded that the electrolytic reduction of β-anthraquinone sulfonic acid proceeds as indicated on the preceding page.

In the near future experiments will be conducted to reduce anthraquinone dyes to their respective "vats" electrolytically.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 24, 1924, Dr. C. J. Thatcher in the Chair.

THE ELECTROLYTIC PREPARATION OF METANILIC ACID AND ITS COMMERCIAL POSSIBILITIES.[1]

By Arthur K. Doolittle[2].



METANILIC ACID.

Abstract.

The possibility of developing a continuous commercial method for the manufacture of metanilic acid of uniform purity suggested the investigation of an electrolytic reduction. The factors influencing the course and extent of the electrolysis were considered to be: electrode material, electrolyte, concentration of depolarizer, current density, temperature, and catalytic agents. Of these, the effect of temperature, current density, and concentration of depolarizer were investigated, and the results are reported below. The yield was found to increase with both rise in temperature and in current density, but there was no increase in efficiency with increased concentration of depolarizer. The analytical determination of the yield by titration with $NaNO_2$ solution presented considerable difficulty, due to the length of time required for the diazotization in dilute solutions. A method of titrating simultaneously from two burettes—one into the amine, and the other into pure acidulated water—was found to eliminate most of the error due to loss of HNO_2 during the diazotization.

INTRODUCTION.

1. The Material.

Properties. Metanilic acid, $C_6H_4NH_2SO_3H$,1 : 3, is a brown to violet colored crystalline powder (white when pure). It is easily

[1] Manuscript received June 15, 1923. Thesis submitted in partial fulfillment of the requirements for the Degree of Chemical Engineer, Columbia University, New York, N. Y.

[2] Present address: Care, Dorr Co., Westport, Conn.

dried and is not at all deliquescent. Its specific gravity in water is greater than one, though the dried solid is quite fluffy and bulky. The anhydrous acid crystallizes in long fine needles, while, with slow evaporation, monoclinic crystals are formed containing 1.5 mols H_2O.[3] The acid has a very large temperature coefficient of solubility. At 7° 100 cc. H_2O dissolves 1.276 g. of the anhydrous acid, at 15°, 100 cc. H_2O dissolves 1.47 g., while at 100°, the acid is extremely soluble—a boiling solution continuing to dissolve large quantities without becoming saturated.

Metanilic acid decomposes when heated so that no melting point is obtainable, but it is readily converted into the amide, melting point 142°, by the standard methods.[4]

Uses. Metanilic acid is used as an intermediate in the manufacture of many dyes, among which may be mentioned the following: Monazo dyes: metanil yellow, acid yellow; disazo dyes: cotton orange R, sulfon black 3B, sulfoncyanine, napthalene acid black; triphenylmethane dyes; agalma green B; sulfur dye; cotton black. Of these, metanil yellow $C_6H_4\begin{cases}SO_3Na\\N = N - C_6H_4NHC_6H_5\end{cases}$ finds the widest application. It is rather more yellow in color than its isomer orange IV, (sulfanilic acid + diphenylamine) and is used in wool dyeing in spite of its poisonous nature. Its chief employment, however, is in paper dyeing (wall paper), carpet printing, and coloring varnishes.[5] In 1912, 181,411 lb. of metanil yellow, valued at $218,060, was sold. Only 90,385 lb. of the dye was produced, however, during this year. The production during the war was large, reaching a maximum in 1920 with 629,437 lb.

2. *Its Manufacture.*

Chemistry of Manufacture. Metanilic acid is at present made by reducing the *m*-nitrobenzene-sulfonic acid obtained either by sulfonating nitrobenzene, or by nitrating benzene-sulfoinc acid. In either case, the meta compound predominates, and the proportion of ortho and para isomers is about 10 per cent.

In practice, the *m*-nitrobenzene-sulfonic acid is generally made by sulfonating nitrobenzene. Reduction is effected by the use of

[3] Beilstein II p. 568.
[4] Mulliken (1922) IV p. 14, Test 4.10.
[5] Georgievics and Grandmougin, Dye Chemistry (1920) p. 102.

cast iron borings, and for this operation, the *m*-nitrobenzene-sulfonic acid is not isolated but the excess acid in the sulfonation serves, after dilution, to generate the hydrogen for the reduction. The equations follow:

$$C_6H_5NO_2 + H_2SO_4 : SO_3 \rightarrow C_6H_4NO_2SO_3H + H_2O$$

$$C_6H_4NO_2SO_3H + 3Fe + 3H_2SO_4 \rightarrow C_6H_4NH_2SO_3H + 3FeSO_4 + 2H_2O$$

$$xH_2SO_4 + 2C_6H_4NH_2SO_3H + (x + 1)\ Ca\ (OH)_2 \rightarrow (C_6H_4NH_2SO_3)_2\ Ca + xCaSO_4$$

$$(C_6H_4NH_2SO_3)_2\ Ca + Na_2CO_3 \rightarrow 2C_6H_4NH_2SO_3Na + CaCO_3$$

$$C_6H_4NH_2SO_3Na + HCl \rightarrow C_6H_4NH_2SO_3H + NaCl$$

3. Possibilities of Improvement.

Comparative theoretical costs. The theoretical cost of reduction per lb. metanilic acid by the chemical method is as follows:

1 mol metanilic acid = 3 mols iron.

$$\begin{array}{cc} 173 & 3 \times 55 \times 8 \\ 1 & 0.97 \end{array}$$

Hence, iron costs $0.97 \times \$0.01 = \$0.0097$ per lb. metanilic acid.

The theoretical cost of reduction per lb. metanilic acid by the electrolytic method is as follows:

1 mol metanilic acid = 6×96500 coulombs.

Voltage at lead electrodes = 2.2 v. Hence kw-hr. consumed per lb. metanilic acid is—

$$\text{Kw-hr.} = \frac{6 \times 96500 \times 2.2 \times 454}{1000 \times 3600 \times 173} = 0.93 \text{ kw-hr. per lb. metanilic acid.}$$

With electricity at $0.01 per kw.-hr. the cost of reduction would be $0.0093 per lb. metanilic acid operating at 100 per cent efficiency.

Practically, an excess iron is used over the theoretical in the chemical reduction, and in the electrolytic reduction, 100 per cent current efficiency would never be realized.

It appears, then, that theoretically there is little to be saved on electrolytic reduction over the chemical method. This is due, primarily, to the fact that no new acid has to be used for the latter, the only cost being that of the iron.

Increased Purity of Product. Electrolytic methods generally allow better regulation of conditions. Hence, it is often the rule that electrolytic chemicals are obtained in a higher degree of purity than those made by chemical methods. In the manufacture of dye intermediates, perhaps more than with any other chemicals, absolute uniformity of product is essential. This does not necessarily mean absolute purity, but there could be no better assurance of uniformity than a high standard of purity. The question of making intermediates up to a standard of uniformity introduces a large amount of expense that does not appear in a process cost analysis. A batch that does not come up to specifications is a total loss, and it is probably to this one factor alone that the wide difference between apparent cost of manufacture and selling price of metanilic acid is due.

An electrolytic process that would turn out an absolutely uniform product from day to day would effect a great saving in the cost of manufacture of this material.

Decreased Labor in a Continuous Process. The chemical reduction as used at present is a batch process. A reaction of this type cannot readily be adapted to continuous operation. Most electrolytic processes, on the other hand, are conducted on a large scale by continuous methods.

It is evident, then, that the possibilities for improvement are considerable, and that, while the cost of the reduction itself will not be much reduced by use of the electric current, this item is comparatively small in comparison with the other factors discussed.

We may divide the field of electrolysis of organic compounds into two classes[6]:

A. The compound is itself an electrolyte and conducts the current with its own ions. Such is the case with the electrolysis of esters of dibasic acids by the method of Brown and Walker as familiar examples.

[6] Löb-Lorenz, Electrochemistry of Organic Compounds (1906).

B. The compound is not an electrolyte, and the oxidation or reduction becomes a secondary action. The conduction of the current must be provided for by the addition to the solution of an electrolyte, such as an inorganic acid, base, or salt. The ions of the electrolyte, carrying their charges, migrate to the electrodes where they are discharged, and then react with the organic compound. Thus the organic material acts as a depolarizer. This class of reaction is more frequent than the first in organic electrochemistry.

The reaction between the depolarizer and the discharged ion must take place in the thin film adjacent to the electrode. It is within this narrow sphere of action that the reaction velocities determining the course of the reduction must be controlled.

There are little means offered for controlling the concentration of the depolarizer in this region, except those of using suitable solvents, proper temperatures, and thorough agitation. The concentration of the discharged ion, however, can be controlled by (a) current density, (b) concentration of electrolyte, and (c) electrode potential.

To get complete reduction of the nitro group of nitrobenzene to the amino group requires a very high reduction velocity, combined with very low condensation velocity and a trifling rearrangement velocity. This points to high current density and overvoltage, and an acid solution, but not sufficiently concentrated acid to favor the molecular rearrangements. While the results for aniline formation perhaps do not apply *in toto* to the reduction to metanilic acid, they serve as a guide in the study of the reduction of the latter.

THE EXPERIMENTAL PROBLEM.

Outline of the Problem and Method of Attack.

The development of an improved commercial process for the manufacture of metanilic acid appears desirable and offers considerable possibilities. The lines wherein an improvement seems most essential are in the matter of producing an absolutely uniform product from day to day, and in the development of a continuous process to replace the batch methods now in use. While theoretically, the cost of reduction is about the same by either the chemical method (iron) or by the electrolytic method (assuming 100 per

cent. efficiency in both cases) the consideration of the other possibilities above mentioned made a study of the electro-reduction to metanilic acid seem advisable.

Factors Influencing Electrolysis. The literature on the reduction of aromatic nitro-compounds is quite extensive, but, oddly enough, only one piece of experimental work on the electro-reduction to metanilic acid has come to the attention of the writer,[7] and this is only a meager paragraph with no reference to details. A study of the general literature on the reduction of nitro-bodies, however, points to the use of a dilute acid solution, the use of lead electrodes, and an elevated temperature as favoring the complete reduction to the amine.

The factors influencing electrolysis which it seemed most essential to consider are:

1. Electrode material and physical state.
2. Character and concentration of electrolyte.
3. Concentration of depolarizer.
4. Current density.
5. Temperature.
6. Catalytic agents.
7. Agitation or circulation of electrolyte.

In order to get some co-ordinate relation between these variable factors, it is obviously necessary to vary only one factor at a time. It was originally intended to make a complete series of experiments which would show the effect of the variation of each one of the above mentioned factors, but difficulties in the determination of yields narrowed the scope of the investigation to the determination of the effects of only numbers 3, 4, and 5 above.

Datum Conditions. A set of datum conditions were chosen to serve as a primary reference plane in correlating the effects of the various factors. For this purpose, a combination of conditions was taken which seemed most reasonable from the study of the literature. These were:

1. Lead electrodes. Later a sponge lead surface was given to the cathode.
2. 10 per cent H_2SO_4 for both catholyte and anolyte.
3. Depolarizer concentration 10. g./L. or 0.045 M.
4. Cathode current density = 0.125 amp./sq. dm.
5. Temperature 70° C.

[7] Haussermann, Chem. Zeit. **17**, 129, 209 (1893).

When the results of the effect of temperature and current density were determined, a new set of datum conditions was established and the effect of concentration of depolarizer was then investigated. The secondary reference plane was then:

1. Sponge lead cathode.
2. 10 per cent H_2SO_4 for catholyte.
3. Depolarizer concentration 10 g./L.
4. Cathode current density = 0.38 amp./sq. dm.
5. Temperature 80°.

Two runs were also made at a current density of 0.5 amp./sq. dm. and at a temperature of 85-88° C.

Determination of Yields. The yields were determined by a volumetric method which was far from satisfactory, but perhaps as accurate as any method that has been worked out for the estimation of amines. This is the method of titiration with a standard solution of $NaNO_2$, which works so admirably in the determination of sulfanilic acid. The difficulties, both theoretical and practical, are described below.

A copper coulometer was employed and the following data were recorded for each run:

1. Datum conditions. The constancy of these conditions for each run was checked by periodic readings of current, voltage and temperature.
2. Volume of catholyte before run.
3. Time of run till hydrogen evolution was apparent. (Calculated on the basis of current strength and weight of depolarizer).
4. Gain in weight of coulometer.
5. Volume of cathode solution after run.
6. Results of analysis.

Additional data were taken when occasion demanded.

From the above data, the material efficiency and the current efficiency were calculated for each run, and these results plotted against the variable factor for each group of runs. Thus, a correlation of the curves of the several groups should disclose the effect of the variation of each factor upon the production of metanilic acid.

EXPERIMENTAL WORK.

Preparation of the Starting Material. The calcium salt of meta-nitrobenzene-sulfonic acid was used for the starting material.

Ten pounds of the calcium salt were prepared by sulfonating

nitrobenzene, neutralizing with milk of lime, and concentrating the filtrate. The lime water was carefully added, and the proper amount determined by analysis, in order not to introduce unnecessarily impurities into the product. The product which crystallized out from the cooling of the concentrated filtrate was purified by recrystallization from alcohol. A considerable portion of the crude material was insoluble in alcohol. An examination of the residue showed it to consist almost entirely of an organic salt of calcium, which we took to be an isomer of *m*-nitrobenzene sulfonate, formed in small amounts simultaneously with the meta acid during the sulfonation. The recrystallized product (soluble in alcohol) was the calcium salt of *m*-nitrobenzene sulfonic acid, sufficiently pure, when dried, for the purposes of this investigation.[8]

Set-up of the Cell. The cell (Fig. 1.) was made with a lead cathode bent into a hollow 4-sided prism, with openings or slits at the top and bottom to permit circulation of the catholyte. About the cathode was an electro-filtrous diaphragm which separated the cathode space from the surrounding anode chamber. Lead anodes on each of the four walls of the square-based glass jar completed the cell proper. Within the cathode space was inserted a glass serpentine through which water could be circulated, and the cathode liquor was thoroughly agitated by a glass stirrer running at about 200. r. p. m. The cell was mounted on an electric hot-plate, and quite satisfactory temperature control was obtained in the cathode chamber by the combined effects of the electric hot-plate and the cooling coils.

The current was provided by a low voltage generator of quite constant characteristics, and was led to the cell through a copper coulometer, an ammeter, and suitable resistances. A voltmeter was connected to the cell terminals to record the potential drop across the cell.

The Reduction. Before each run, the cathode solution of the cell was made up by dissolving a weighed quantity of depolarizer in a known volume of 10 per cent H_2SO_4. The exact acid content was then checked by a titration and a measured volume of the warm solution—usually 600 cc.—taken. In the meantime the cell

[8]Elbs, Electrolytic Preparations, p. 86.

was being heated, and when the proper temperature was attained, the pickling solution (10 per cent H_2SO_4) was siphoned out of the cathode space, and the hot solution containing the depolarizer introduced. The current was then switched on immediately, and the temperature regulated to the proper point by the cooling water in the glass coils.

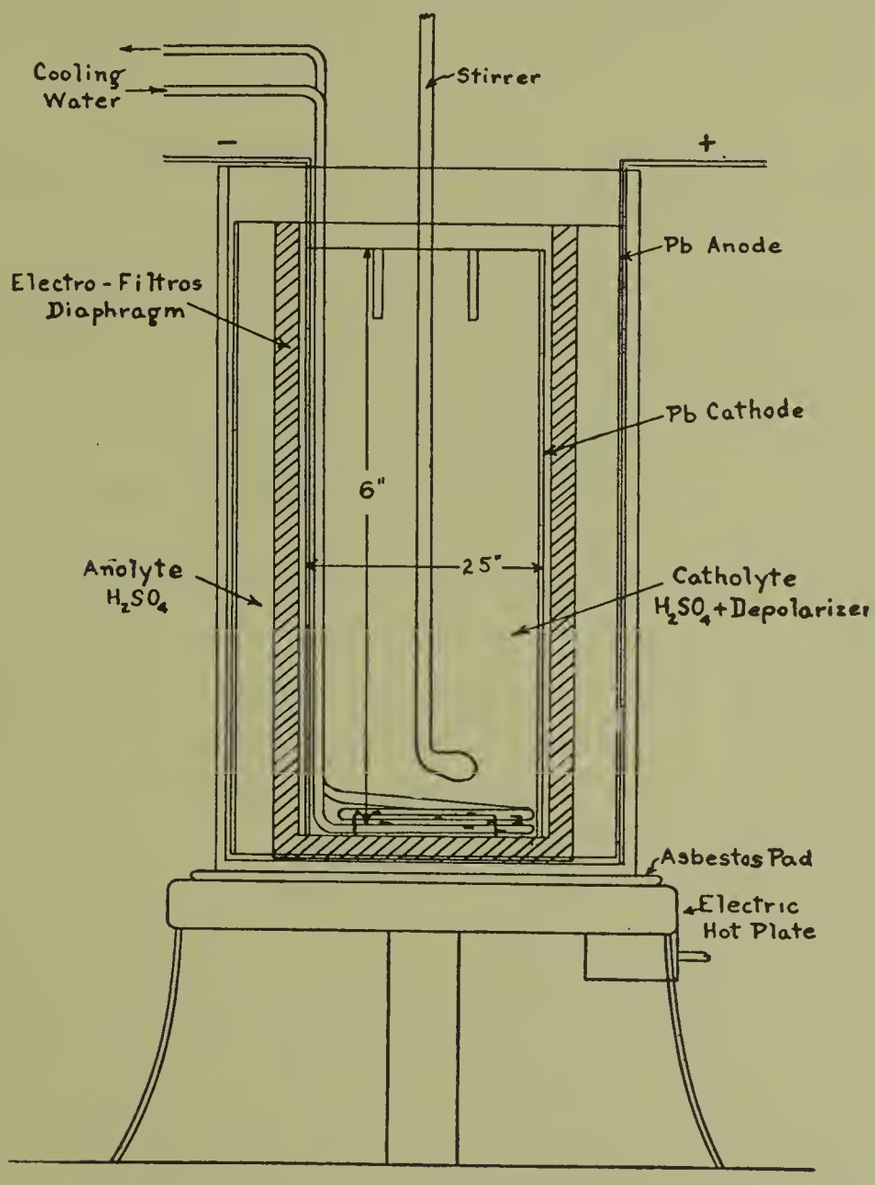


FIG. 1. Cell for reduction of $C_6H_4NO_2SO_3H$ to metanilic acid.

The reduction was continued under constant conditions for each run for a length of time calculated on the basis of the current strength and weight of depolarizer taken, and checked in most cases in practice by the appearance of H_2. The first hydrogen evolution generally appeared a little before the calculated end point, but the evolution never became rapid until after the calculated number of coulombs had passed.

After the run was stopped, the cathode liquor was immediately siphoned off and the volume measured. In the cases where a high concentration of depolarizer was used, the samples for analyses were pipetted out at once before the material had a chance to crystallize out from cooling.

The chemistry of the reduction consists in the replacement of the oxygen by hydrogen according to the following reaction:

$$C_6H_4SO_3HNO_2 + 6H^+ \rightarrow C_6H_4SO_3HNH_2 + 2H_2O + 6\oplus$$

Hence, 1 mol metanilic acid corresponds to the absorption of 6 faradays or 6 × 96,500 coulombs.

The Analysis. As mentioned above, the yield of metanilic acid was determined in each case by a titration with $NaNO_2$ solution. Starch + KI paper was used as an external indicator.

In carrying out the diazotization, a low temperature was maintained by the use of ice in the early experiments, but later, it was observed that there was no error introduced in working at room temperatures while operating with our dilute solutions. This is easily understood when we consider that even though the diazonium compound may decompose at ordinary temperatures, the amount of HNO_2 necessary to complete the diazotization will not be affected thereby, but will depend only on the amount of amine originally present.

The accurate determination of sulfanilic acid by the diazotization method is well established. In fact, the standardization of $NaNO_2$ solution is often done by titration against this acid. But in the case of sulfanilic acid, the influence of the SO_3H group in the para position accelerates the velocity of diazotization to such a point that the end point is quickly reached. The influence of a group in the ortho position is even greater, but in the *m*-position, it is slight.[9] Dilution also retards the velocity of diazotization.[10]

In the titrations involved in these analyses, the method, obviously, was to add a small portion of the $NaNO_2$ solution at a time—say 0.5 cc.—until the end point was approached when the size of the increments was reduced. A moment's calculation will show that

[9] Boeseken, Brandsma, and Schoutissen, Proc. Acad. Sci. Amsterdam **23**, 249-66 (1920).

[10] E. Tassilly, Bul. Soc. Chim. **27**, 19-23 (1920).

this results in a very dilute solution of the nitrite when near the stoichiometrical neutral. For example, suppose we are titrating in a volume of 100 cc. and a fresh 0.5 cc. portion of the 0.05 molar nitrite solution is added. The concentration of $NaNO_2$ in this mixture will then be: $0.5 \times 0.05 \times 100/1{,}000 = 0.00025$ molar. This is the maximum concentration of $NaNO_2$. As the diazotization approaches 100 per cent, this concentration falls off rapidly.

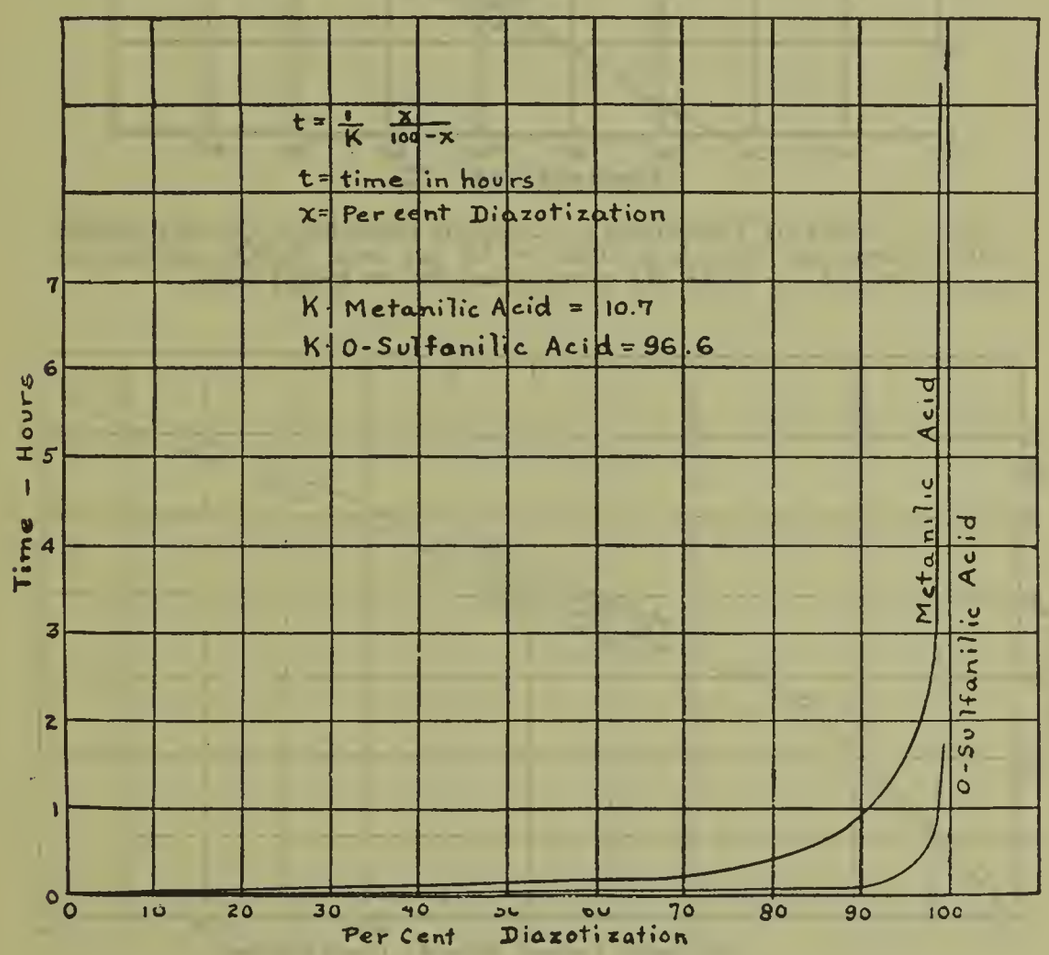

t = 1/K · x/(100−x)
t = time in hours
x = Per cent Diazotization
K = Metanilic Acid = 10.7
K = O-Sulfanilic Acid = 96.6
Time - Hours
Per Cent Diazotization
Metanilic Acid
O-Sulfanilic Acid

FIG. 2. Curves showing velocity of diazotization of metanilic acid and of *o*-sulfanilic acid in solution 0.002 molar with respect to both HNO_2 and the amine.

Due to these effects, there is an apparent shifting of the end point in the titration of metanilic acid, which was the source of much trouble in the estimation of the product. Reference to the curves in Fig. 2, showing the velocity of diazotization of 0.002 molar solutions of nitrous acid and amine, (data from [9] [10] [11]) indicates that 9 hr. would be required for a single diazotization to 99 per cent. But in the titrations as carried out in these analyses,

[11] Tassilly, Compt. Rend. **157**, 1148-50; **158**, 335-8; **158**, 489-91.

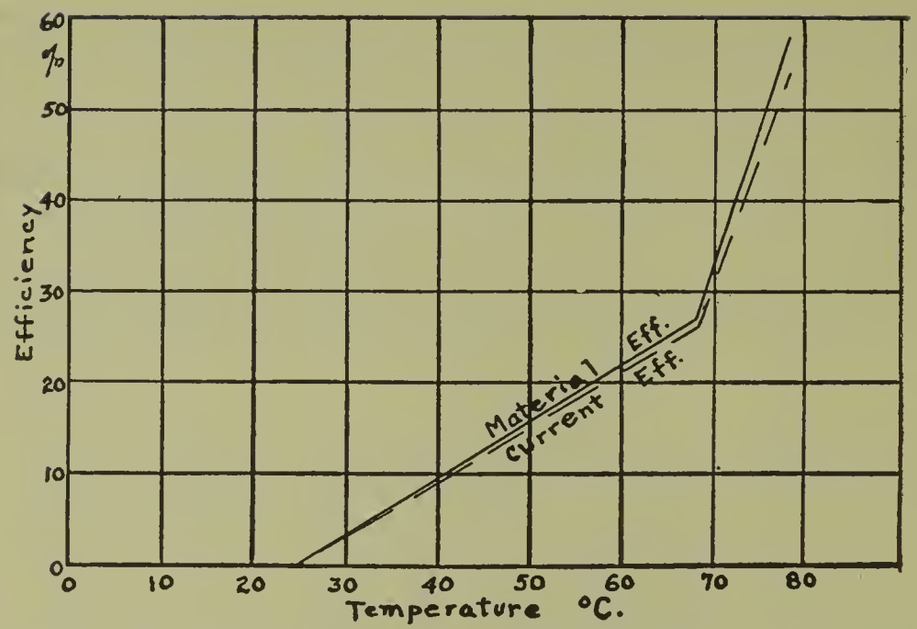


FIG. 3. Effect of Temperature. Constant conditions: Current density = 0.125 amp./sq. dm.; acid conc. = 10 per cent H_2SO_4; depolarizer conc. = 10 g./L. or 0.045 M; cathode material = bright lead.

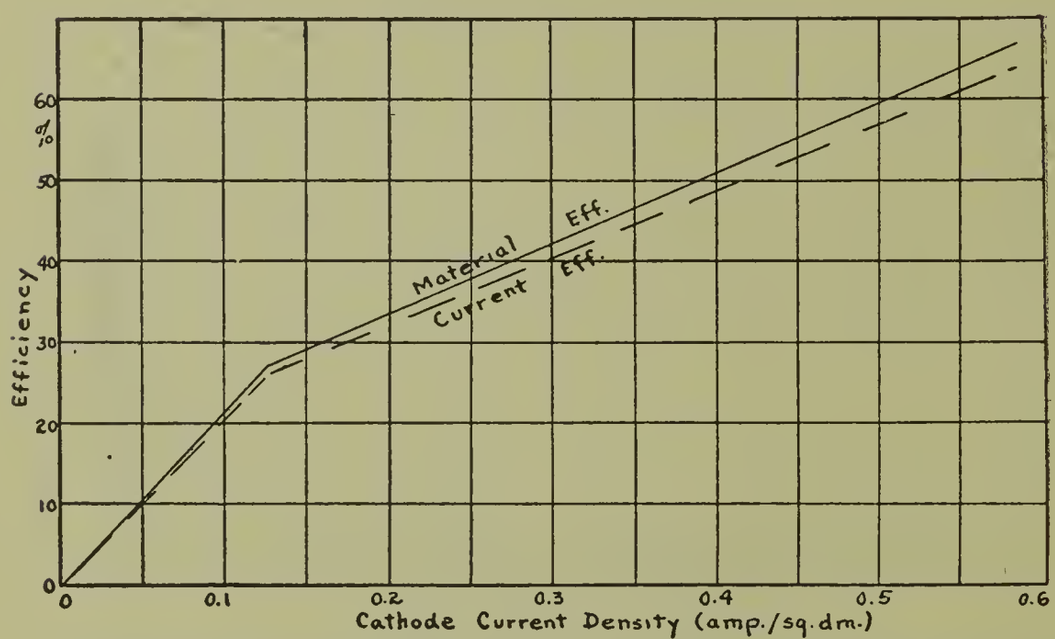


FIG. 4. Effect of Current Density. Constant conditions: Temperature = 70°; acid conc. = 10 per cent. H_2SO_4; depolarizer conc. = 10 g./L. or 0.045 M; cathode material = bright lead.

we are continually working up to an end point (100 per cent diazotization) at very low concentrations. Hence to reach even 90 per cent diazotization at each addition would require a long time.

Now while the titration is proceeding so slowly, there will be noticeable loss of HNO_2, both by volatilization from the solution, and by atmospheric oxidation, and the extent of the loss will be

affected by the amount of stirring, temperature, and time of titration. These losses, of course, destroy the precision of the titration, and a great deal of trouble was experienced at first in getting any sort of check results.

The method finally adopted was to titrate simultaneously from two burettes, one into the sample from the cathode solution, and the other into pure acidulated water. By stirring each the same

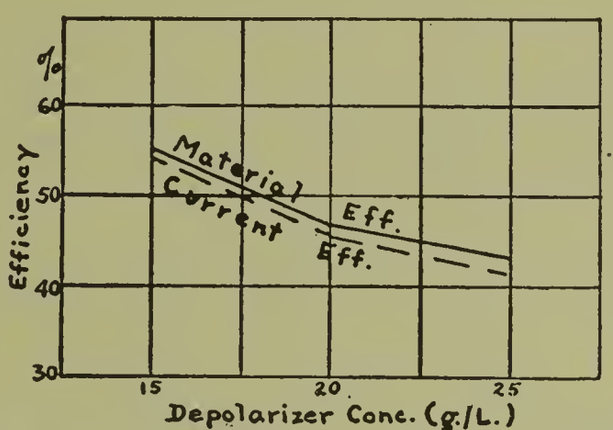


FIG. 5. Effect of Concentration of Depolarizer. Constant conditions: Temperature = 80°; current density = 0.38 amp./sq. dm.; acid conc. = 10.1 per cent; cathode material = sponge lead.

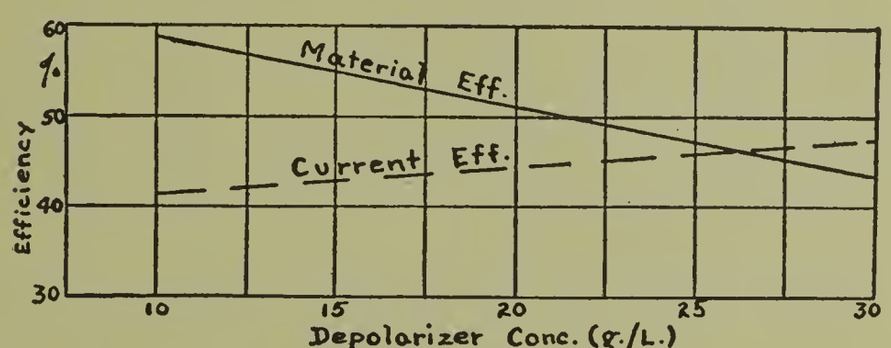


FIG. 6. Effect of Concentration of Depolarizer. Constant conditions: Temperature = 85-88°; current density = 0.5 amp./sq. dm.; acid conc. = 10.1 per cent; cathode material = sponge lead.

amount, and running each the same length of time, the losses above referred to should be quite the same in each. The diazotization was considered complete when both end points shifted at about the same rate. Then the difference in the two burette readings gave the $NaNO_2$ used up in the diazotization. This method gave fairly concordant results, but invariably took from 12 to 15 hr. for completion. The accuracy of the titration cannot be considered better than 1 per cent by volume.

Results. Ten reduction runs with the conditions so arranged as to bring out the effects of variation of the various factors were

made and analyses completed. In addition to these, two runs were made in an attempt to carry out a simultaneous sulfonation and reduction, starting with nitrobenzene in concentrated H_2SO_4 solution. These sulfonation experiments were not successful, the product in each case being *p*-amido-phenol-*m*-sulfonic acid.

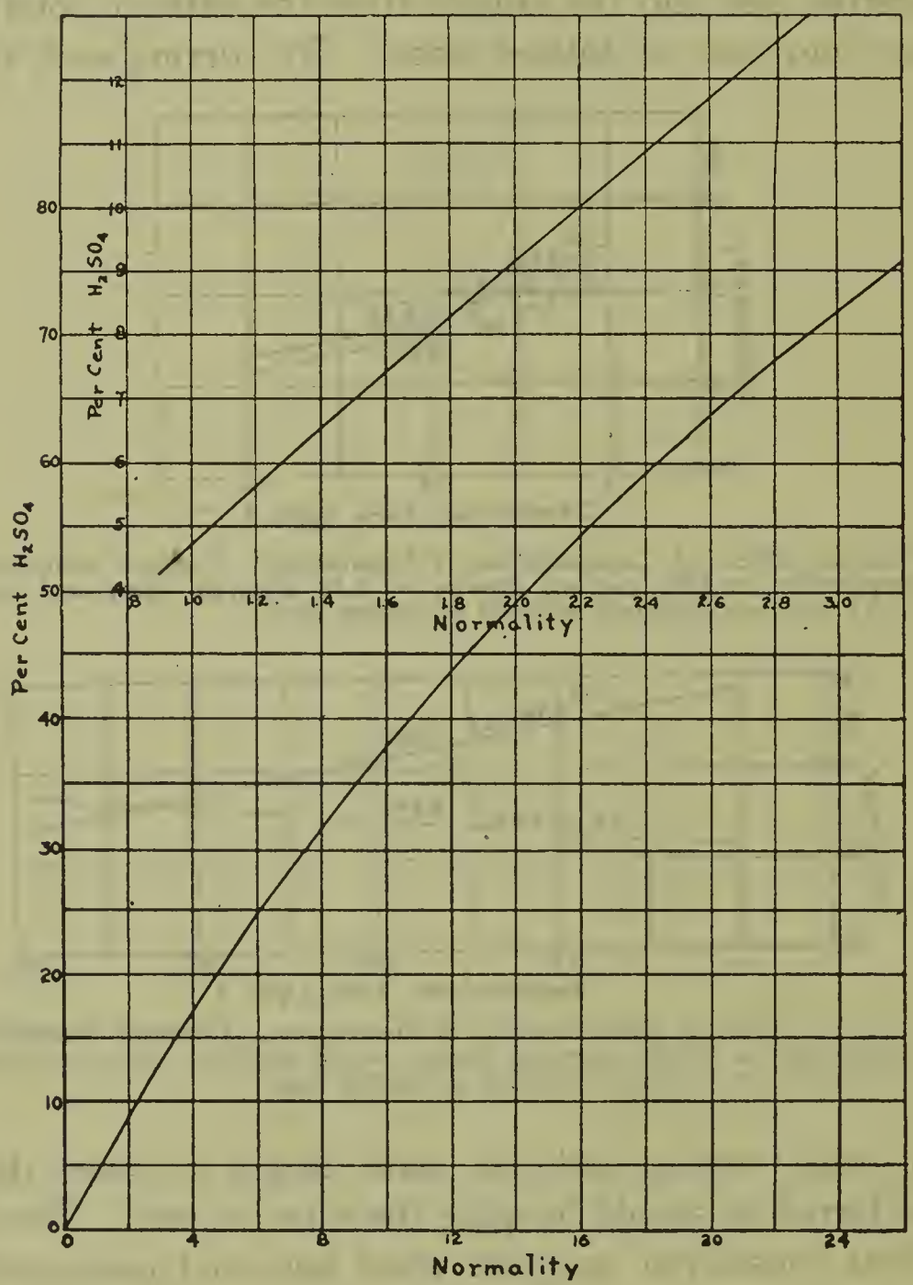


FIG. 7.

The reduction runs were made using as the starting material the calcium salt of *m*-nitrobenzene sulfonic acid, $C_6H_4NO_2SO_3Ca\frac{1}{2}$ molecular weight 222, crystallized from alcohol and dried in air.

The anode liquor was 10 per cent H_2SO_4 and the anodes were lead plates, total exposed area 5 square decimeters. The cathode space had a volume of 600 cc., and the cathode liquor was

the depolarizer in solution in 10 per cent H_2SO_4. The cathode area immersed (both sides) was 7.75 sq. dm. The other dimensional data may be taken from the diagram of the cell, Fig. 1.

The concentration of the acid in the catholyte was checked before each run by a titration with standard alkali. This was converted to percentage figures with the aid of the curve, Fig. 7.

The collected results of the reduction runs are recorded in Table I.

TABLE I.

The Reduction of Metanilic Acid

Run	Cathode Current Density Av. Amp./ sq. dm.	Temp. °C.	Depolarizer Conc. g./L.	H_2SO_4 Acid Conc. Per Cent	Time of Run		Mat. Yield Mols	Mat. Eff. Per Cent	Curr. Eff. Per Cent
					Hr.	Min.			
1	0.537	58	25	10	5		0.0045	6	3*
2	0.127	66	10	10	4	35	0.00726	27	26
3	0.121	24	10	10	4	42	.....	0	0
4	0.123	78	10	10	4	5	0.013	58	54
5	0.585	71	10	10	1	..	0.0181	67	64
6	0.50	85	10	10	1	20	0.0133	59	41†
7	0.373	82	15	10	2	20	0.0225	56	55
8	0.379	80	20	10	3	5	0.0255	47	46
9	0.39	80	25	10	3	45	0.0293	43	42
10	0.504	88	30	10	3	5	0.0354	44	47‡

* Not accurate—material in suspension when measured out.
† Increased current density and temp.
‡ Increased current density, temp., and conc. of depolarizer.

Analyses of solid, precipitated from cathode solutions of runs No. 9 and No. 10 on cooling, showed 20 per cent metanilic acid in former and 18 per cent in latter. From these data, the following groupings were made to show the effect of the variation of one factor at a time.

Effect of Temperature.

Constant conditions.

Current density = 0.125 amp./sq. dm. av.
Acid conc. = 10 per cent H_2SO_4.
Depolarizer conc. = 10 g./L. or 0.045 M.
Cathode material = Bright lead.

Variable factor and effect.

Temp. °C	Material Eff. Per cent	Current Eff. Per cent
24	0	0
66	27	26
78	58	54

See curves Fig. 3.

Effect of Current Density.

Constant Conditions.

Temp. = 70° av.
Acid conc. = 10 per cent H_2SO_4.
Depolarizer conc. = 10 g./L. or 0.045 M.
Cathode material = Bright lead.

Variable factor and effect.

Current Density	Material Eff.	Current Eff.
0	0	0
0.127	27	26
0.585	67	64

See curves Fig. 4.

Effect of Depolarizer Concentration (Second Datum Plane.)

Constant Conditions.

Temp. = 80°
Current density = 0.38 amp./sq. dm.
Acid conc. = 10.1 per cent.
Cathode material = Sponge lead.

Variable factor and effect.

Conc. of Depolarizer	Material Eff.	Current Eff.
15	56	55
20	47	46
25	43	42

See curves Fig. 5.

Effect of Depolarizer Concentration (Third Datum Plane).

Constant Conditions.

Temp. = 85-88°
Current density = 0.5 amp./sq. dm.
Acid conc. = 10.1 per cent.
Cathode material = Sponge lead.

Variable factor and effect.

Conc. of Depolarizer	Material Eff.	Current Eff.
10	59	41
30	44	47

See curves Fig. 6.

In the last three runs, since concentration of dissolved material was above that required for saturation at room temperature, there was considerable crystallization of the reduced mixture upon cooling.

Discussion of Results. As only a part of the various relationships have been investigated so far no final conclusions can be drawn in regard to the possibilities of the electrolytic reduction. However on the basis of results which are presented herewith, we note (see Fig. 3) that there is no appreciable reduction at room temperatures, but that the amount of reduction increases with rise in temperature. From Fig. 4, it appears that the yield increases with increased current density at low concentrations of depolarizer. Fig. 5 indicates a reduction in efficiency with increased concentration of depolarizer, though, of course, the actual material yield is increasing. In run No. 10, the combination of high temperature, high current density and high depolarizer concentration was tried, with the results indicated on Fig. 6. This is apparently in contradiction with the results of Fig. 3 and 4. A possible explanation of this is the following: analyses were made by withdrawing a 25 cc. sample of the cathode solution and titrating it with $NaNO_2$ solution. The difficulties referred to in connection with the analyses would throw the burden of error on the side of a too low result. Now the more concentrated the solution, the greater will be the actual error in the result caused by the same percentage error in the analysis. Then if the aliquot portion is multiplied to include the whole volume of the solution, it is evident that the total error in the concentrated solutions is much greater than in the dilute solutions. Following this reasoning, it is quite possible that the actual reduction efficiencies at 0.5 amp./sq. dm. and depolarizer conc. of 30 g/L. are considerably higher than the 45 per cent indicated on Fig. 6.

The results obtained in these experiments are not satisfactory enough to warrant adaptation of the electrolytic method to a commercial process, but the problem should not be considered as impossible of solution since the effects of the variation of electrode material, electrolyte, and catalytic agents have not yet been exhaustively investigated.

Even 50 per cent efficiency could be profitably employed in a

continuous process for the manufacture of metanilic acid, if a method could be devised to separate the pure product from the rest of the solution so as to give an absolutely uniform product, but no satisfactory method has been discovered up to the present time. The solubility characteristics of both metanilic acid and *m*-nitrobenzene sulfonic acid are similar. Both are comparatively insoluble cold and very soluble hot, so that the precipitate that crystallizes out on cooling contains the solids in about the same proportion as that for the solution. This is borne out in the results of the analyses of the precipitates of runs No. 9 and No. 10. A product containing only 20 per cent metanilic acid would, of course, be unsuitable for a dye intermediate.

SUMMARY

The properties and uses of metanilic acid have been presented. It has been shown that the development of a continuous process for making a product of uniform purity would have wide commercial possibilities. The theoretical cost of the reduction by the chemical and electrolytic methods has been shown to be about the same, on the basis of 100 per cent reduction.

The results of the experimental work indicate that

1. Increase in temperature increases yield.

2. Increase in current density increases yield.

3. Increase in concentration of depolarizer shows no increase in efficiency.

4. The solid crystallizing from concentrated solutions of the reduced liquor contains only a small proportion of metanilic acid.

No satisfactory commercial method for the production of metanilic acid can be devised on the basis of these preliminary results.

ACKNOWLEDGMENT

The encouragement, helpful criticism and advice offered by Dr. Colin G. Fink under whose direction this investigation was carried out is gratefully acknowledged. The writer also wishes to express his indebtedness to Dr. C. J. Thatcher, who suggested the problem, for his many helpful suggestions and much valuable time in following the progress of the experimental work.

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Electrochemical Laboratories,
Columbia University,
New York City.

DISCUSSION.

C. J. THATCHER[12]: If we can determine roughly the percentage of metanilic acid which will be formed by the electrolytic reduction, I believe that a commercial method for the production of metanilic acid can be easily worked out, because there are a great number of electrolytic conditions that have not yet been studied. What are the possibilities of improving the yield that the author has obtained? Can anyone suggest how a 99 per cent yield of metanilic acid can be obtained?

ALEX. LOWY[13]: I would like to look into it. You see you are getting an NH_2 group, and if you get a compound with NH_2 you could not couple that with an aldehyde and get a precipitate. On page 70, the catholyte had a volume of 600 cc. Was the depolarizer soluble in 10 per cent sulfuric acid? If the electrolyte you started with was the calcium salt of nitro-benzene-sulfonate, do you not get a precipitate of calcium sulfate?

ARTHUR K. DOOLITTLE: There was a slight cloudiness in the solution, but, of course, as far as the nitro group is concerned, the reduction would be the same whether calcium sulfate were present or not.

ALEX. LOWY: Do you think that, perhaps, something besides an acid medium would be better?

ARTHUR K. DOOLITTLE: We only tried reducing an acid solution. We had not planned using other solvents, so that I am not in a position to state whether I think that would be more satisfactory or not. Most of the more satisfactory results obtained in the reduction of nitro-benzene were in acid solutions. We followed that as a lead.

C. J. THATCHER: Mr. Doolittle found only a very slight percentage of by-products. The problem seemed to resolve itself then into finding the conditions for a better current yield. The material yield would be all right if we could get it all reduced to metanilic acid. Further investigation seems well worth while. There will be no difficulty in separating metanilic acid from the raw material

[12] Chem. Engr. and Electrochemist, New York City.
[13] Prof. of Organic Chemistry, Univ. of Pittsburgh, Pittsburgh, Pa.

if its concentration becomes high enough, and that is merely a matter of sufficiently far extended reduction.

W. C. MOORE[14]: A number of years ago when I was a student at the University of Chicago, I carried out some experiments on the formation of organic amalgams with Dr. H. N. McCoy. One of those which we isolated was tetramethyl ammonium amalgam. We did not succeed in getting the least trace of tetramethyl ammonium amalgam until we went from an aqueous to an *absolute alcohol solution.* Much work has been done on using other solvents than water in organic reactions. We know, for instance, that anhydrous formic acid and anhydrous hydrogen cyanide are good ionizing agents; also that nitrobenzene is a fair one and I know that absolute eythl alcohol is a very good one. Absolute ethyl alcohol today can be secured, as you all know, if necessary, in tank car lots; so that it would seem wise in these organic reactions to change solvents occasionally, to see what results are obtained.

C. J. BROCKMAN[15]: Would the conductivity of alcohol warrant its use? What electrolyte are you going to use along with alcohol?

W. C. MOORE: If you remember, the conductivity of water is not very high. You are probably referring to the dielectric constant. You must, of course, use electrolytes that are soluble in alcohol. In the case to which I referred our electrolyte was tetramethyl ammonium chloride, and it was moderately soluble in absolute alcohol.

C. SCHALL[16] (*Communicated*): I should like to suggest that further experiments be carried out in cylindrical instead of rectangular cells, in order to insure a more uniform action of the current between, and at the surface of, the electrodes.

According to McMaster and Wright,[17] *m*-nitrobenzol sulfonic acid is not soluble. Would it not be possible, therefore, to cool Doolittle's solution after electrolysis and extract the nitrobenzolsulfonic acid with ether, and thus determine approximately the

[14] Research Chemist, U. S. Industrial Alcohol Co., Baltimore, Md.
[15] University of Georgia, Athens, Ga.
[16] Physical Chemical Lab., Leipzig Univ., Leipzig, Germany.
[17] J. Amer. Chem. Soc., **40**, 683 (1918).

amount of amido acid formed? This method, if applicable, would be more rapid than the titration method used by Doolittle.

Curves in Fig. 4 and 6 indicate that in spite of the same concentration of the depolarizer and the same current density (0.5 amp. per sq. dm.) the current efficiency is higher with smooth lead electrodes than with spongy lead (even when the temperature of the electrolyte with spongy lead electrodes is higher). Since a similar observation has been made in the reduction of menthone at smooth and rough lead cathodes,[18] and since the current efficiency was much higher with *cadmium cathodes* than with lead cathodes in the reduction of menthone to menthane, is it not probable that a cadmium cathode would be more efficient than a lead one in the reduction of *m*-nitrobenzol sulfonic acid to *m*-amido-sulfonic acid? Cadmium as cathode is not readily corroded in dilute sulfuric acid-alcoholic solutions.

ARTHUR K. DOOLITTLE: I have consulted the article by McMaster and Wright referred to by Prof. Schall, but did not find mention of the ether solubility of *m*-nitrobenzene sulfonic acid. Accordingly, I determined, roughly, the ether solubility of this acid myself. The sample used for this determination was purchased from the Eastman Organic Chemical Labratories, and was carefully dried *in vacuo*. Dried ether was saturated with the acid at 21° C., and the weight contained in 10 cc. of the solution determined after evaporation of the ether. The solubility thus obtained was 9.9 g./100 cc. ether, at 21° C.

The water solubility of *m*-nitrobenzene sulfonic acid is 4.35 g./100 g. H_2O, at 21° C., according to Beilstein, II, p. 125. If we take the coefficient of partition of this acid between water and ether to be, from these figures, about 0.435, it can be readily shown it will take over 40 extractions, each with 50 cc. ether from 1 liter of aqueous solution containing 30 g. of the acid to effect a 99 per cent extraction. That is, to equal the accuracy of my titrations by the method suggested would necessitate over 40 extractions under the most favorable conditions, which is scarcely an improvement over the method used.

[18] Schall and Kirst, Zeitsch. f. Elektrochem., **1923**, 537.

A modification of Van Slyke's method for the determination of amino nitrogen by measuring the nitrogen gas evolved has been suggested by Mrs. Doolittle as an alternative to the titration method which I used. From the least quantity of metanilic acid obtained in any of my runs, 0.0045 mols, there would be obtained over 100 cc. of nitrogen after diazotization and decomposition of the diazonium salt, and the determination of this quantity of gas with an accuracy of 1 per cent would be simple. The advantage of the method lies in the use of an excess of the nitrite, thus increasing the velocity of the diazotization and enabling the analysis to be completed in a comparatively short time.

Referring to the last paragraph of Prof. Schall's discussion, I would say that the data support the conclusion that the current efficiency is higher with smooth lead electrodes than with sponge lead, and I am indebted to Prof. Schall for calling attention to this fact. It is quite possible, too, that a cadmium cathode might prove more efficient than lead, though we were unable to test out the effect of variation of electrode material, as originally planned, in the time at our disposal after a satisfactory method of analysis had been worked out.

The instantaneous current efficiency during a reduction decreases as the reduction proceeds, due to the starting material being used up, and the material yield, of course, increases. The best commercial process then ought to be at an economic balance between the decrease in the over-all current efficiency and the increase in the total material yield when we are dealing with a material such as this, that is high in cost of raw material, but high in value when finished. What I mean is, that the cost of the material is a large item compared with cost of the electricity consumed. Therefore, the economic balance between the cost of the material and the cost of the electricity is the determining factor in a commercial process; and in connection with the idea of possibly following the reaction as it proceeds by measuring the nitrogen given off, if we were to use the Van Slyke method that I have just suggested, we could in that way determine the instantaneous current efficiencies by plotting the curve of yield against ampere

hours. It is my idea that some method could be worked out involving these ideas and give us a better determination of the best commercial process.

COLIN G. FINK[19]: Referring to Prof. Schall's comments regarding the spacing of the electrodes, as a matter of fact, we took that into account, and the spacing of the electrodes was practically uniform throughout, even though a square cell was used and not a cylindrical one.

[19] Head, Division of Electrochemistry, Columbia Univ., New York City.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 24, 1924, Dr. C. J. Thatcher in the Chair.

THE ELECTROLYTIC OXIDATION OF PARA-NITROTOLUENE AND PARA-CHLOROTOLUENE TO THEIR RESPECTIVE ACIDS.[1]

By Raymond F. Dunbrook[2] with Alexander Lowy.[3]

Abstract.

The electrolytic oxidation of *p*-nitrotoluene and *p*-chlorotoluene to the corresponding acids has been carried out in nitric acid solution of 20 to 30 per cent concentration, with use of platinum electrodes. For the electrolytic oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid the optimum conditions were, a temperature of 100° C., with a current density of 4 amp. per sq. dm., using 20 per cent nitric acid solution as anolyte. The yield in this case was 34.1 per cent of the acid. For the oxidation of *p*-chlorotoluene to *p*-chlorobenzoic acid the best results were obtained with platinum anode, a temperature of 100° C. and a current density of 0.5 amp. per sq. dm. and 20 per cent nitric acid solution, using glacial acetic acid as a solvent.

Part I.

The Electrolytic Oxidation of Para-Nitrotoluene to Para-Nitrobenzoic Acid.

The objects of this investigation were: First, to find out if *p*-nitrobenzaldehyde could be prepared by the electrolytic oxidation of *p*-nitrotoluene, under the conditions found favorable by Perkin[4] for the electrolytic oxidation of toluene to benzaldehyde; Second,

[1] Manuscript received December 10, 1923.

[2] This report represents a part of a thesis presented by Raymond F. Dunbrook in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1923.

[3] Contribution from the Department of Chemistry, Univ. of Pittsburgh, Pittsburgh, Pa.

[4] Trans. Faraday Soc. **1**, 31 (1905); Chem. News, **91**, 54 (1905); Chem. News, **92**, 66 (1905); Moser and Haber "Die Elektrolytischen Processe der Organischen Chemie," p. 73 (1910).

to prepare *p*-nitrobenzoic acid from *p*-nitrotoluene by the electrolytic oxidation of the latter; Third, to investigate the use of nitric acid as electrolyte in organic electrochemical work.

Elbs[5] in 1896 succeeded in oxidizing *p*-nitrotoluene to *p*-nitrobenzyl alcohol electrolytically. Starting with 15 g. of *p*-nitrotoluene he obtained 1-2 g. of unchanged *p*-nitrotoluene, 7 g. of *p*-nitrobenzyl alcohol, together with 0.1-0.5 g. of an insoluble body and a little tar. This represents about a 40 per cent yield, based on the *p*-nitrotoluene used with a current efficiency of about 30 per cent.

Fichter[6] recently repeated Elbs' work and obtained from 15 g. of *p*-nitrotoluene in acetic acid 4.5 g. of unchanged *p*-nitrotoluene, 1.5 g. of tarry product, 3 g. of *p*-nitrobenzyl alcohol, 0.7 g. of *p*-nitrobenzyl-acetate, 0.18 g. of a compound melting at 170° (the ether of *p*-nitrobenzyl alcohol) and 0.5 g. of *p*-nitrobenzaldehyde which was identified by its melting point and that of its phenylhydrazone derivative. He further found that *p*-nitrobenzyl alcohol itself was readily oxidized to *p*-nitrobenzoic acid, with a 50 per cent yield and a current efficiency of 16 per cent and that, with the use of *p*-nitrobenzaldehyde as starting material, an almost quantitative yield of the acid was obtained, with a current efficiency of 16 per cent.

Fichter's work showed that the electrolytic oxidation of *p*-nitrotoluene suspended in sulfuric acid gives mainly *p*-nitrobenzoic acid, but in very small yields, while with the use of acetic acid as solvent, the main product is the alcohol. The acetic acid thus seems to act as a protective agent against the further oxidation of the alcohol.

Coehn[7] claims to have obtained *p*-nitrobenzoic acid from *p*-nitrotoluene with the use of a lead peroxide anode in place of platinum, but gives no data to substantiate his claim. Fichter in his article makes mention of Coehn's remark and states that the yields of *p*-nitrobenzoic acid were less with lead peroxide anodes.

According to a German patent,[8] the addition of 0.1 g. of manganese sulfate acting as oxygen carrier in Elbs' process serves to carry the oxidation to *p*-nitrobenzoic acid. No yields are, however, given.

[5] Zeit. f. Elektrochem. 2, 522 (1896).
[6] Helvetica Chimica Acta 3, 396 (1920).
[7] Zeit. f. Elektrochemie 9, 643 (1903).
[8] D. R. P. No. 117,129 (1900); Friedländer 6, 112 (1900).

Fichter[9] also carried out an experiment in which the acetic acid was replaced by acetone. 15 g. of *p*-nitrotoluene in 80 g. of acetone were mixed with 2 g. of concentrated sulfuric acid and 7 g. of water. The solution was electrolyzed at room temperature. Besides 3 g. of unchanged *p*-nitrotoluene, 0.13 g. of *p*-nitrobenzyl alcohol and 2.5 g. of tarry matter were obtained.

Experimental Part.

According to the literature, no one has studied in detail the electrolytic oxidation of substituted toluene derivatives such as *p*-nitrotoluene, under conditions similar to those employed by Perkin in the electrolytic oxidation of toluene to benzaldehyde. Experiments were, therefore, carried out, in which *p*-nitrotoluene, dissolved in acetone and sulfuric acid, was electrolyzed. Only insignificant amounts of the aldehyde resulted from this work, but small amounts of *p*-nitrobenzoic acid were obtained. The results of this work are tabulated in Table I.

Electrolytic Oxidation of Para-Nitrotoluene in Nitric Acid.

As far as can be found in the literature, there is no mention made of the use of nitric acid in organic electrolytic oxidations. The use of nitric acid is, however, recorded in connection with the electrolytic nitration of naphthalene.[10] The authors have found a case in which the electrolytic oxidation in nitric acid of concentration insufficient to bring about chemical oxidation, proceeds smoothly and with a fair current efficiency for organic electrochemical experiments.

A sketch of the apparatus used in this work is shown in Fig. 1. This apparatus consisted of an ordinary wide mouth bottle of one liter capacity. A cork of good grade was fitted to the bottle, through which were bored five openings, for the stirrer, porous cup exit, thermometer, condenser and anode. The porous cup was fitted with a glass tube, which led directly into the air. With this precaution, there was no danger of the hydrogen and oxygen mixing in the cell. A 45° adapter passed through the stopper, and was attached to a reflux condenser. Some difficulty was encountered in keeping the stopper from being destroyed by the fumes

[9] Helvetica Chimica Acta 3, 396 (1920).
[10] D. R. P. No. 100,417, March 10, 1897.

of the oxides of nitrogen and nitric acid, which were produced in the electrolysis. However. when the apparatus was all assembled and before inserting the stopper into the bottle, it was given a heavy coat of collodion, and this protected the stopper fairly well, but left much to be desired.

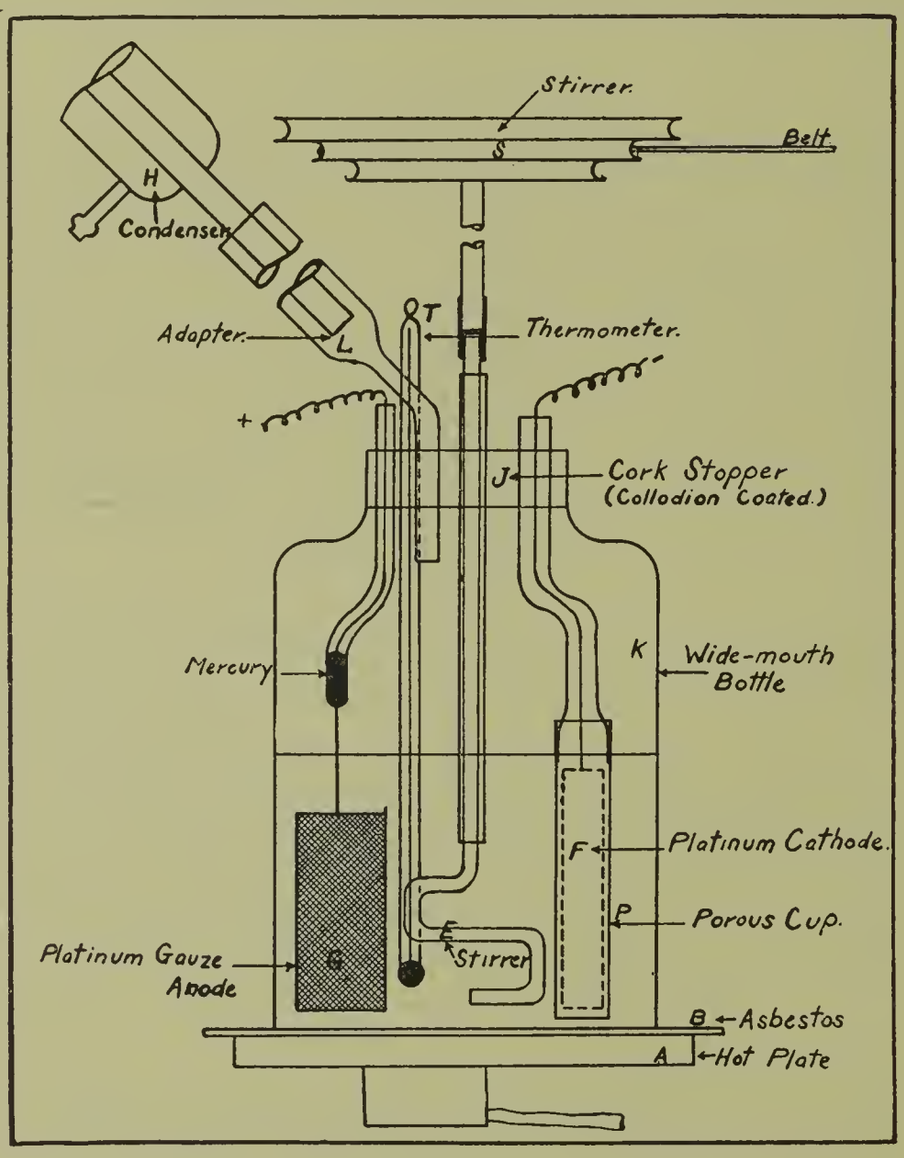

FIG. 1

One experiment will be described in detail (Experiment 12). Fifteen g. of *p*-nitrotoluene was placed in the wide mouth bottle; 300 cc. of 20 per cent nitric acid were next added, and the stopper holding anode, cathode, stirrer, thermometer and adapter was next inserted. The condenser was next attached to the adapter and all joints were sealed with collodion. The temperature was next brought to 100° by the hot plate. The electrolysis was continued for 9 amp.-hr. After the electrolysis, the stopper was

removed, and all parts were carefully washed into the cell with hot water. The contents of the cell were then transferred to a one-liter long-neck, round-bottom flask and distilled with steam. The *p*-nitrotoluene being volatile with steam, passed over together with some nitric acid. When all *p*-nitrotoluene had passed over, the hot residue in the flask was filtered and cooled to 15° C. The white *p*-nitrobenzoic acid separated and was removed by filtration with suction. The filtrate was evaporated to 50 cc. and yielded about 0.15 g. more of *p*-nitrobenzoic acid. The acid thus obtained melted at 230°-235° C. By dissolving it in $NaHCO_3$ solution, filtering and acidifying, the acid which reprecipitated, melted at 235-236° C. The *p*-nitrobenzoic acid was further identified by reducing to *p*-aminobenzoic acid, having a melting point of 186° C. The distillate from steam distillation was filtered, and the recovered *p*-nitrotoluene was dried and weighed. A series of experiments was conducted, the results of which are tabulated in Table II, a discussion of which follows.

Experiments A, B and C show the results of blank experiments. In these experiments, the apparatus was assembled exactly as for the electrolytic experiments and the solution was vigorously stirred and heated at 100° for 4.5 hr. The *p*-nitrotoluene was then steam distilled and the residue filtered and cooled but no acid separated on cooling. This work was checked several times and in no case was any *p*-nitrobenzoic acid produced, thus proving that the concentration of nitric acid employed was insufficient to bring about chemical oxidation. When no current was employed, the nitric acid solution remained perfectly clear and no brown fumes were evident above the solution. When the current was passed, however, the solution at the end of the electrolysis always had a lemon-yellow color, was clear and contained no tarry matter.

A series of experiments was conducted at a temperature of 90° and with the use of 25 per cent nitric acid as anolyte and catholyte. The results of these experiments are shown in Fig. 2. The curve has a maximum in the vicinity of a point corresponding to a current density of 4 amp. per sq. dm. Even at this current density, the gas evolution at the anode was quite pronounced, and the space above the solution was dark brown with NO_2 fumes. On increasing the current density to 6 amp. per

sq. dm., there is a slight decrease in the current efficiency, and at a current density of 8 amp. per sq. dm., there is a further drop in the current efficiency. At current densities of 6 and 8 amp. per sq. dm., the oxygen evolution at the anode had markedly increased, and the space above the solution had a deep brown color due to oxides of nitrogen. When the current density was decreased to 2 amp. per sq. dm., the current efficiency decreased, there was almost no gas evolution and very little color above the liquid. The above results are tabulated in Table II, in experiments 1-4, inclusive.

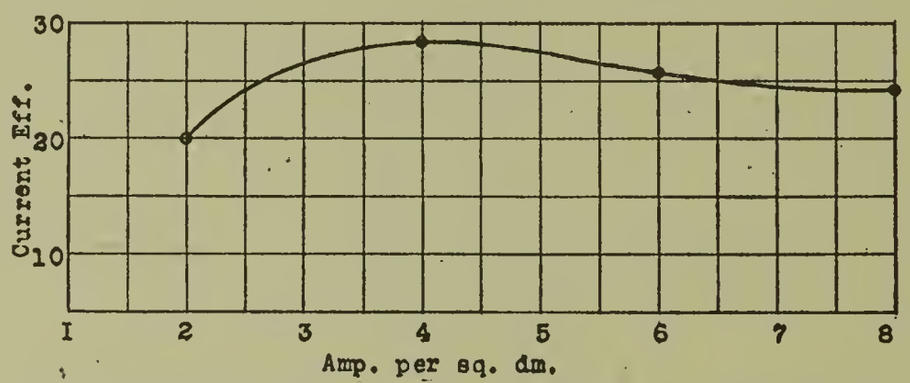

FIG. 2. Current efficiency-current density curve. No solvent. Temperature, 90° C. Anolyte, 25 per cent nitric acid.

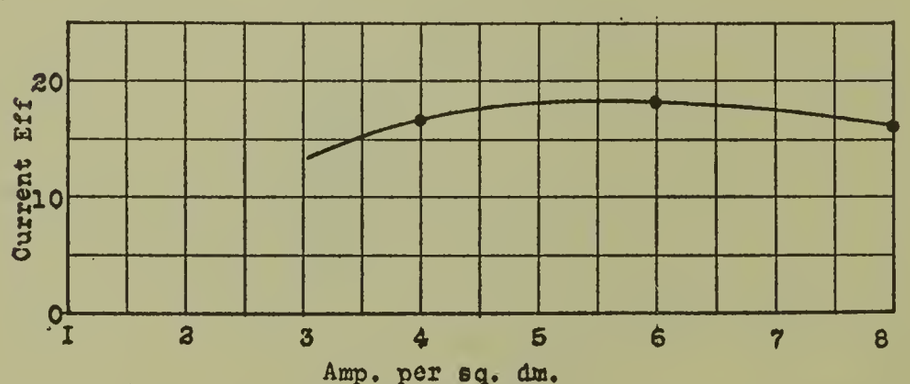

FIG. 3. Current density-current efficiency curve. Acetic acid used as solvent. Temperature, 90° C. Anolyte, 25 per cent nitric acid.

The above experiments 2, 3 and 4 were repeated with the use of acetic acid as solvent, and are recorded in experiments 5, 6 and 7. In Fig. 3, the results are plotted. The best results were obtained with a current density of 6 amp. per sq. dm., the current efficiency in this case being 18.2 per cent. The difference between these experiments and the ones without the acetic acid was that all the *p*-nitrotoluene was in solution, and the gas evolution at the anode was almost negligible. The amount of *p*-nitrobenzoic

acid obtained was less than without the acetic acid, which can probably be accounted for by assuming that some of the acetic acid was decomposed, thus decreasing the current efficiency in the oxidation of *p*-nitrotoluene.

Another set of experiments was conducted, using the best current density of 4 amp. per sq. dm. and a concentration of 25 per cent HNO_3, but varying the temperature. The results are plotted in Fig. 4, and are recorded in experiments 2, 8, 9 and 10.

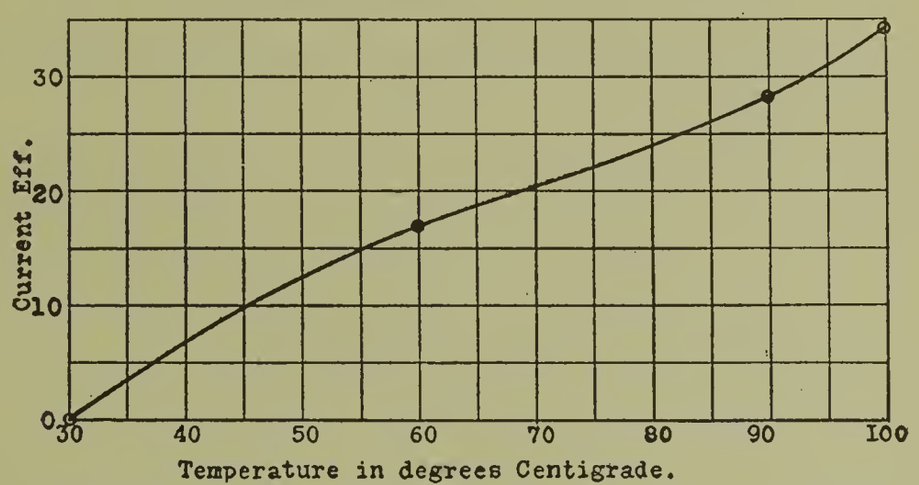

FIG. 4. Current efficiency-temperature curve. Time, 4.5 hr. Current density, 4 amp. per sq. dm.

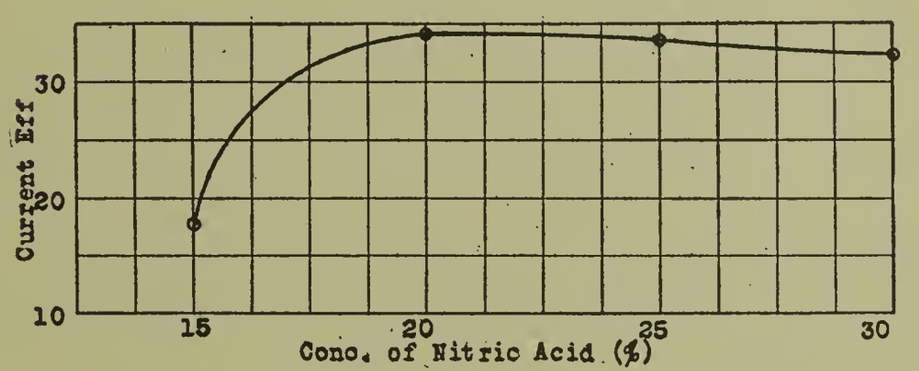

FIG. 5. Current efficiency-concentration curve (HNO_3). Temperature 100° C. Time, 4.5 hr. Current density, 4 amp. per sq. dm.

The current efficiency decreases very rapidly with a decrease in temperature and is almost a linear function of the temperature. The maximum current efficiency of 33.1 per cent was obtained at 100° C. while at 30° C. no *p*-nitrobenzoic acid was obtained.

Still another set of experiments was conducted, using the best temperature of 100° C. and the best current density of 4 amp. per sq. dm. and varying the concentration of nitric acid. Above 20 per cent nitric acid, the concentration had only a slight effect

on the current efficiency, but a slight decrease was obtained at concentrations of 25 and 30 per cent nitric acid. When 15 per cent nitric acid was used as anolyte, the current efficiency dropped to 17.6 per cent. These results are tabulated in experiments 10, 11, 12 and 13 and are plotted in Fig. 5.

Thus the best conditions for the electrolytic oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid were found to be the following: the use of 20 per cent nitric acid as anolyte and catholyte, with a temperature of 100° C. and a current density of 4 amp. per sq. dm. In all of the above experiments 15 g. of *p*-nitrotoluene were used in the anolyte.

Experiment 16 was conducted with an increased concentration of *p*-nitrotoluene. In this case 50 g. of *p*-nitrotoluene were suspended in 300 cc. of 20 per cent nitric acid using the optimum conditions in the electrolysis. There was no increase in the amount of *p*-nitrobenzoic acid. With the use of the optimum conditions, but without the diaphragm, the results were almost the same as with the diaphragm, and the diaphragm can, therefore, be dispensed with. The results are shown in experiments 14 and 15.

Two other electrodes were also used in this study, viz: duriron and carbon. Experiment 17 gives the results with the use of duriron as anode. Only a small quantity of *p*-nitrobenzoic acid was obtained with duriron, probably due to the low overvoltage of oxygen on duriron. The results with carbon electrodes (experiment 18) were negative, and gave no acid. The solution turned dark brown during the electrolysis, and the carbon electrodes were vigorously attacked.

Experiment No. 19 was carried out in which the optimum conditions were used, but the time was doubled, current being passed for 18 amp.-hr. The yield was increased to 4.9 g. of *p*-nitrobenzoic acid, but this is not in proportion to the time, based on a 9 amp-hr. experiment.

The probable theory of the electrolytic oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid may be summarized as follows: Since non-electrolytic experiments show that nitric acid solutions of 20 and 25 per cent nitric acid do not oxidize *p*-nitrotoluene to *p*-nitrobenzoic acid at 100° C., and that when the current is passed oxida-

tion of *p*-nitrotoluene to *p*-nitrobenzoic acid does take place, either the concentrated nitric acid liberated at the anode or the oxides of nitrogen formed by the decomposition of this produced nitric acid at 100° C. or the oxygen produced at the pole brings about the oxidation. It is probably a combination of the concentrated nitric acid produced at the anode together with the oxygen produced that bring about the oxidation.

SUMMARY OF PART I.

1. Eleven experiments were carried out on the electrolytic oxidation of *p*-nitrotoluene in acetone and sulfuric acid solutions.

2. At temperatures of 15° C. only insignificant amounts of *p*-nitrobenzaldehyde are formed, but small amounts of *p*-nitrobenzoic aicd are formed as a result of the oxidation.

3. Twenty-one experiments were carried out on the electrolytic oxidation of *p*-nitrotoluene in nitric acid solution of concentration insufficient to bring about chemical oxidation.

4. It has been shown that *p*-nitrobenzoic acid can be produced by the electrolytic oxidation of *p*-nitrotoluene in HNO_3 solution at temperatures above 60° C. with platinum anode.

5. The best conditions found for the oxidation are the use of 20 per cent nitric acid, a temperature of 100° C. and a current density of 4 amp. per sq. dm. with platinum anode, giving a current efficiency of 34.1 per cent.

6. A diaphragm can be dispensed with in the oxidation in nitric acid solution.

PART II.

The Electrolytic Oxidation of Para-Chlorotoluene to Para-Chlorobenzoic Acid.

This phase of the work was undertaken to study the electrolytic oxidation of other para substituted toluene derivatives in nitric acid solution. *P*-chlorotoluene was chosen because there is no reference given in the literature pertaining to the electrolytic oxidation of it.

The experiments were conducted in the apparatus shown in Fig. 1, and the results of this work are tabulated in Table III.

The details of an experiment as described under Part I were closely adhered to. In place of 15 g. of *p*-nitrotoluene, 15 cc. of *p*-chlorotoluene (sp. gr. 1.07) were used, and after the electrolysis, the *p*-chlorotoluene was distilled with steam, the residue filtered and cooled to 15° C. *P*-chlorobenzoic acid is even less soluble in water than *p*-nitrobenzoic acid. Most of the *p*-chlorobenzoic acid was not in solution, and was thus separated on filtering the hot liquid. The remainder of the *p*-chlorobenzoic acid separated from the mother liquor on cooling to 15° C. The *p*-chlorobenzoic acid was purified by dissolving in sodium bicarbonate solution and reprecipitating with hydrochloric acid. The acid melted at 235° C.

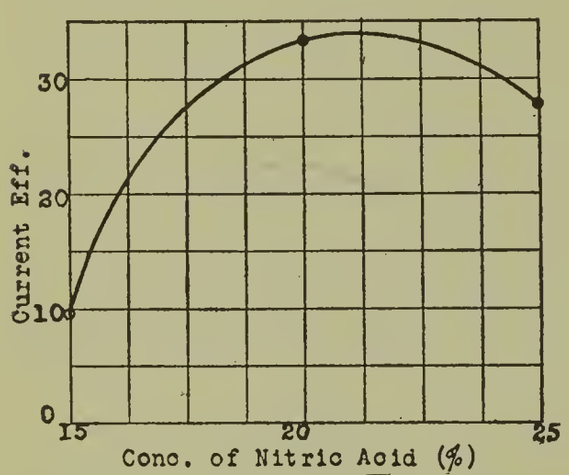

FIG. 6. Current efficiency-concentration curve (HNO_3). Temperature, 100° C. Current density 4 amp. per sq. dm.

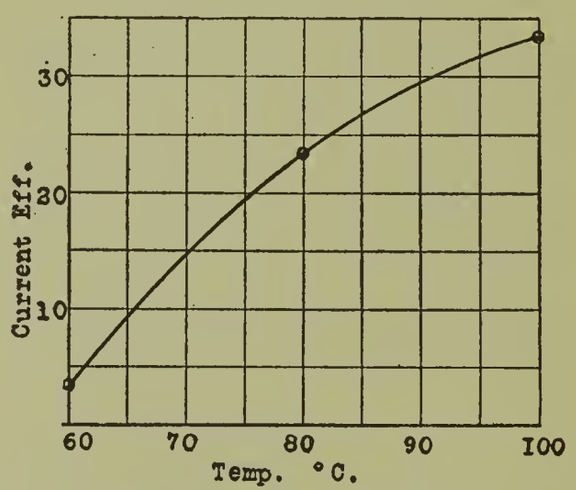

FIG. 7. Current efficiency-temperature curve. Anolyte, 20 per cent nitric acid. Time 4.5 hr. Current density, 4 amp. per sq. dm.

The *p*-chlorobenzoic acid produced was further identified by preparing the amide having a melting point of 170° C., and by the methyl ester having a melting point of 43° C.

Three blank experiments were carried out with 20 per cent nitric acid, and the results are shown in experiments A, B and C. In experiment A, 15 cc. of *p*-chlorotoluene were suspended in 300 cc. of 20 per cent nitric acid, and heated to 100° C. for 4.5 hr. The *p*-chlorotoluene was then steam distilled and the residue was cooled, when 0.07 g. of *p*-chlorobenzoic acid separated. In experiment B, the time of the blank experiment was increased to 9 hours, and 0.61 g. of *p*-chlorobenzoic acid was produced. In experiment C, the time was increased to 18 hr. and 1.16 g. of *p*-chlorobenzoic acid was produced. Experiment D is a blank with 25 per cent

nitric acid which gave 1.10 g. of *p*-chlorobenzoic acid for 4. 5 hr.

These experiments show that *p*-chlorotoluene is slightly oxidized to *p*-chlorobenzoic acid by 20 and 25 per cent nitric acid at 100° C. A series of experiments was conducted, using the current density which was found to give the best results in the electrolytic oxidation of *p*-nitrotoluene *viz.*, 4 amp. per sq. dm. A temperature of 100° C. was used and the nitric acid concentration was varied. The results are tabulated in experiments 1, 2 and 3, and are plotted in Fig. 6. With 15 per cent nitric acid a low yield of *p*-chlorobenzoic acid was obtained. With 20 per cent nitric acid

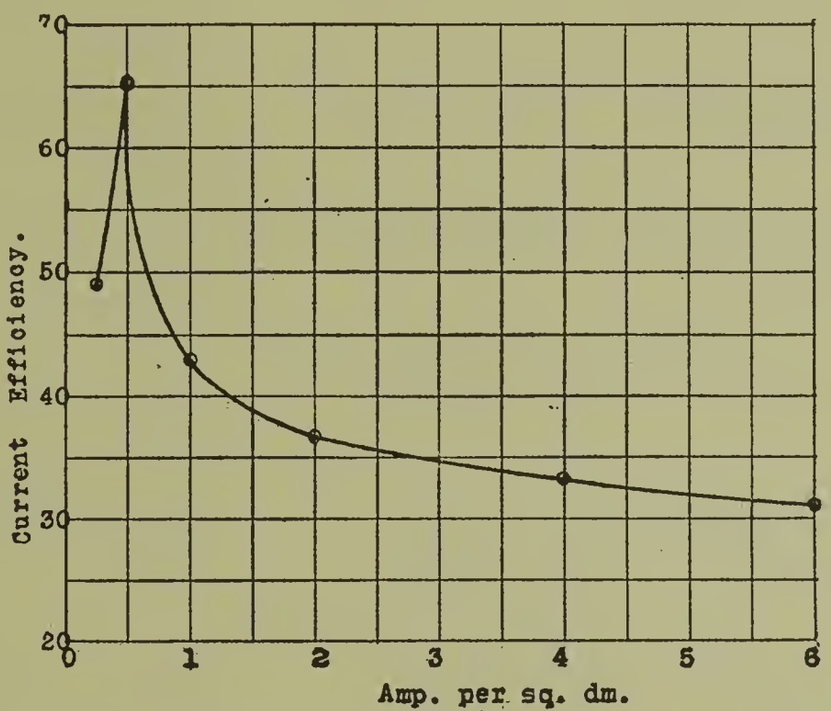

FIG. 8. Current density-efficiency curve. Temperature, 100° C. Anolyte, 20 per cent nitric acid.

the result was better, and with 25 per cent nitric acid, a decrease in yield was obtained, giving a current efficiency of 27.4 per cent. This last experiment with the use of 25 per cent nitric acid was in general not so favorable. Copious brown fumes were evolved above the electrolyte, and after the chlorotoluene was steam-distilled about one gram of yellow gummy substance remained.

A series of experiments was next carried out in which 20 per cent nitric acid was used as the electrolyte with a current density of 4 amp. per sq. dm., and with a variation of the temperature. The experiments were conducted at 100°, 80°, 60° and 40° and are recorded in experiments 2, 4, 5 and 6. The results are plotted in

TABLE I.—*Electrolytic Oxidation of*

Exp.	Object	Anolyte	Catholyte	Anode	Cathode
1	To electrolyze *p*-nitrotoluene in acetone and H_2SO_4	350 cc. acetone: 350 cc. water: 30 cc. H_2SO_4: 10 g. *p*-nitrotoluene	25 cc. 10% H_2SO_4	Platinum sheet: 150 sq. cm.	Platinum rod: 15 sq. cm.
2	Repeat above with lead anode	Same as Exp. 1	25 cc. 10% H_2SO_4	Lead: 150 sq. cm.	Lead: 20 sq. cm.
3	Decrease of current density	Same as Exp. 1	25 cc. 10% H_2SO_4	Platinum: 150 sq. cm.	Platinum: 15 sq. cm.
4	Increased current density	Same as Exp. 1	25 cc. 10% H_2SO_4	Platinum: 150 sq. cm.	Platinum: 15 sq. cm.
5	To try $Ce(SO_4)_2$ as carrier	Same as Exp. 1, plus 5 g. $Ce(SO_4)_2$	25 cc. 10% H_2SO_4	Lead: 150 sq. cm.	Lead: 20 sq. cm.
6	Increase conc. of H_2SO_4 and *p*-nitrotoluene	350 cc. acetone: 350 cc. water: 90 cc. H_2SO_4: 20 g. *p*-nitrotoluene	25 cc. 10% H_2SO_4	Platinum: 150 sq. cm.	Platinum: 15 sq. cm.
7	Use of NaOH as anolyte	350 cc. acetone: 350 cc. water: 20 g. NaOH: 15 g. *p*-nitrotoluene	20% NaOH	Platinum: 150 sq. cm.	Platinum: 15 sq. cm.
8	Use of PbO_2 as anode	350 cc. acetone: 350 cc. water: 30 cc. H_2SO_4: 15 g. *p*-nitrotoluene	10% H_2SO_4	Lead peroxide: 150 sq. cm.	Lead: 20 sq. cm.
9	Use of glacial acetic acid as solvent	350 cc. glacial acetic acid instead of acetone as in Exp. 1	10% H_2SO_4	Platinum: 150 sq. cm.	Platinum: 15 sq. cm.
10	To increase temp.	350 cc. acetone: 350 cc. water: 30 cc. H_2SO_4: 20 g. *p*-nitrotoluene	10% H_2SO_4	Platinum: 150 sq. cm.	Platinum: 15 sq. cm.
11	Lead anode	Same as Exp. 10	10% H_2SO_4	Lead: 150 sq. cm.	Lead: 20 sq. cm.

Para-Nitrotoluene in Sulfuric Acid.

Amp.	Volts	Current Density amp. per sq. dm.	Temp. °C.	Time Hr.	Yield of *P*-nitrobenzoic acid g.	Current Efficiency Per cent	Diaphragm	*P*-nitrotoluene recovered g.	Remarks
2	8	1.33	12-14	6	0.90	7.2	Yes	5	Solution turned dark brown. Isolated small amount of *p*-nitrobenzaldehyde.
2	8	1.33	12-14	6	0.65	5.2	Yes	8	Yield of acid lower than in previous case, but purer.
1.5	6	1	12-14	8	0.95	7.6	Yes	7	Only very slight increase in yield of *p*-nitrobenzoic acid.
4	8	2.66	15	3	0.25	2.0	Yes	4	Increased current density, decreased yield of acid, and increased tarry matter.
2	6	1.33	12	6	0.35	2.9	Yes	7.8	Did not increase yield.
2	5.5	1.33	10	6	0.58	4.6	Yes	17.5	More tarry matter resulted than in Experiment 1. Also yield of acid was decreased.
2	10	1.33	15	6	None	..	No	12	Results very unsatisfactory. No acid obtained.
2	8	1.33	15	6	0.2	1.6	Yes	13	Solution much more colored than with platinum, yield also decreased.
2	8	1.33	15	6	0.35	2.9	Yes	8	Use of acetic acid not as good as acetone.
2	4	1.33	60	6	None	..	Yes	13	Any acid if formed was probably oxidized further to CO_2 and H_2O.
2	6	1.33	60	6	None	..	Yes	16	

TABLE II.—*Electrolytic Oxidation of*

Experiment	Object	Anolyte	Catholyte	Anode	Cathode
A	A non-electrolytic experiment as a blank with diaphragm	300 cc. of 20% HNO_3 and 15 g. *p*-nitrotoluene	20% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
B	Same as Exp. A but no diaphragm	Same as Exp. A	20% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
C	A non-electrolytic blank experiment with 25% HNO_3	300 cc. of 25% HNO_3 and 15 g. *p*-nitrotoluene	25% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
1	Use of HNO_3 as anolyte	Same as Exp. C	25 cc. of 25% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
2	To increase current density	Same as Exp. C	25 cc. of 25% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
3	Same as Exp. 2	Same as Exp. C	25 cc. of 25% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
4	Same as Exp. 2	Same as Exp. C	25 cc. of 25% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
5	Use of glacial acetic acid as solvent	100 cc. acetic acid, 100 cc. water, 75 cc. conc. HNO_3, 15 g. *p*-nitrotoluene	25 cc. of 25% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
6	Same as Exp. 5	Same as Exp. 5	25 cc. of 25% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
7	Same as Exp. 5	Same as Exp. 5	25 cc. of 25% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
8	Lower temp. and no solvent	300 cc. 25% HNO_3, 15 g. *p*-nitrotoluene	25 cc. of 25% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.
9	Same as Exp. 8	Same as Exp. 8	25 cc. of 25% HNO_3	Platinum gauze: 50 sq. cm.	Platinum sheet: 50 sq. cm.

Para-Nitrotoluene in Nitric Acid.

Diaphragm	Amp.	Average Volts	Temp. °C.	Time Hr.	Current Density amp. per sq. dm.	Current Efficiency Per cent	*P*-nitrobenzoic Acid Yield g.	*P*-nitrotoluene Recovered g.	Remarks
Yes	None	None	100	4.5	..	..	None	14.5	With this concentration of HNO_3 no *p*-nitrobenzoic acid was obtained.
No	None	None	100	4.5	..	..	None	14.0	With this concentration of HNO_3 no *p*-nitrobenzoic acid was obtained.
Yes	None	None	100	4.5	..	..	None	14.0	With this concentration of HNO_3 no *p*-nitrobenzoic acid was obtained.
Yes	1	2	90	9	2	20.0	1.88	12.5	Electrolytically some *p*-nitrobenzoic acid was produced.
Yes	2	3.5	90	4.5	4	28.3	2.65	10.7	Increased current efficiency.
Yes	3	5	90	3	6	25.6	2.40	11.3	Decreased current efficiency.
Yes	4	6	90	2.25	8	24.2	2.27	10	Decreased current efficiency.
Yes	2	2	90	4.5	4	16.8	1.58	11	Yield lower than without acetic acid.
Yes	3	3.5	90	3	6	18.2	1.71	11.6	Yield lower than without acetic acid.
Yes	4	5.0	90	2.25	8	16.0	1.50	11.7	Yield lower than without acetic acid.
Yes	2	5.0	30	4.5	4	..	None	14	
Yes	2	4.0	60	4.5	4	17.0	1.6	10.2	

TABLE II.—*Electrolytic Oxidation of*

Experiment	Object	Anolyte	Catholyte	Anode	Cathode
10	To increase temp. and no solvent	300 cc. 25% HNO_3, 15 g. *p*-nitrotoluene	25 cc. of 25% HNO_3	Platinum gauze, 0.5 sq. dm.	Platinum sheet, 0.5 sq. dm.
11	Use of best temp. and current density to vary conc. of HNO_3	300 cc. 15% HNO_3, 15 g. *p*-nitrotoluene	15% HNO_3	Same	Same
12	Same as Exp. 11	300 cc. 20% HNO_3, 15 g. *p*-nitrotoluene	20% HNO_3	Same	Same
13	Same as Exp. 11	300 cc. 30% HNO_3, 15 g. *p*-nitrotoluene	30% HNO_3	Same	Same
14	To try effect of leaving out diaphragm	300 cc. 20% HNO_3, 15 g. *p*-nitrotoluene	20% HNO_3	Same	Platinum wire, 15 sq. cm.
15	Same as Exp. 14	300 cc. 25% HNO_3, 15 g. *p*-nitrotoluene	25% HNO_3	Same	Same
16	To increase conc. of *p*-nitrotoluene	300 cc. 20% HNO_3, 50 g. *p*-nitrotoluene	20% HNO_3	Same	Platinum sheet, 0.5 sq. dm.
17	Use of Duriron as electrode	Same as Exp. 16	20% HNO_3	Duriron, 50 sq. cm.	Same
18	Use of carbon as anode	Same as Exp. 16	20% HNO_3	Carbon rod, 50 sq. cm.	Same
19	To increase time of experiment	Same as Exp. 16	20% HNO_3	Platinum, 50 sq. cm.	Same
20	Use of $NaNO_3$ as anolyte and diaphragm	300 cc. 20% $NaNO_3$, 15 g. *p*-nitrotoluene	20% $NaNO_3$	Same	Same
21	As above and no diaphragm	Same as Exp. 20	20% $NaNO_3$	Same	Same

Para-Nitrotoluene in Nitric Acid (Continued).

Diaphragm	Amp.	Average Volts	Temp. °C.	Time Hr.	Current Density amp. per sq. dm.	Current Efficiency Per cent	*P*-nitro-benzoic acid Yield g.	*P*-nitro-toluene Recovered g.	REMARKS
Yes	2	3.5	100	4.5	4	33.1	3.10	10.3	Increased the current efficiency.
Yes	2	4.5	100	4.5	4	17.6	1.65	10.3	
Yes	2	3.5	100	4.5	4	34.1	3.20	10.2	Best yield obtained.
Yes	2	3.5	100	4.5	4	32.3	3.03	10.3	
No	2	3.0	100	4.5	4	33.0	3.09	10	Result almost as good as with diaphragm.
No	2	2.5	100	4.5	4	33.6	3.15	9.9	Result almost as good as with diaphragm.
Yes	2	2.5	100	4.5	4	33.6	3.15	45.2	Did not increase yield.
Yes	2	2	100	4.5	4	2.4	0.23	42.0	
Yes	2	3.5	100	4.5	4	...	None	43.5	Solution turned dark brown and the carbon anode was attacked.
Yes	2	5.5	100	9	4	26.1	4.90	40.1	Yield was increased but not current efficiency.
Yes	2	6	100	4.5	4	9.8	0.92	10.3	Decided decrease in the acid obtained.
No	2	6	100	4.5	4	...	None	13.5	Solution turned dark brown and became alkaline and a resinous material formed.

TABLE III.—*Electrolytic Oxidation of*

Experiment	Object	Anolyte	Catholyte Per cent HNO_3	Anode	Cathode
A	A non-electrolytic blank experiment	300 cc. 20% HNO_3, 15 cc. *p*-chlorotoluene	20	Platinum gauze, 50 sq. cm.	Platinum sheet, 50 sq. cm.
B	Same as Exp. A	Same as Exp. A	20	Same	Same
C	Same as Exp. A	Same as Exp. A	20	Same	Same
D	Same as Exp. A	300 cc. 25% HNO_3, 15 cc. *p*-chlorotoluene	25	Same	Same
1	Electrolytic experiment with 15% HNO_3	300 cc. 15% HNO_3, 15 cc. *p*-chlorotoluene	15	Same	Same
2	To vary concentration of HNO_3	300 cc. 20% HNO_3, 15 cc. *p*-chlorotoluene	20	Same	Same
3	Same as Exp. 2	300 cc. 25% HNO_3, 15 cc. *p*-chlorotoluene	25	Same	Same
4	To vary the temperature	300 cc. 20% HNO_3, 15 cc. *p*-chlorotoluene	20	Same	Same
5	Same as Exp. 4	Same as Exp. 4	20	Same	Same
6	Same as Exp. 4	Same as Exp. 4	20	Same	Same
7	To vary current density	Same as Exp. 4	20	Same	Same
8	Same as Exp. 7	Same as Exp. 4	20	Same	Same
9	Same as Exp. 7	Same as Exp. 4	20	Same	Same
10	Same as Exp. 7	Same as Exp. 4	20	Same	Same
11	Same as Exp. 7	Same as Exp. 4	20	Same	Same
12	Experiment without diaphragm	Same as Exp. 4	20	Same	Platinum, 15 sq. cm.
13	To try acetic acid as solvent	125 cc. acetic acid, 85 cc. conc. HNO_3, 90 cc. water, 15 cc. *p*-chlorotoluene	20	Same	Same
14	To run a non-electrolytic blank exp. with acetic acid as solvent	Same as Exp. 13	20	Same	Same
15	To increase concentration of *p*-chlorotoluene	300 cc. 20% HNO_3, 50 cc. *p*-chlorotoluene	20	Same	Same

Para-Chlorotoluene in Nitric Acid.

Diaphragm	Amp.	Average Volts	Temp. °C.	Time Hr.	Current Density amp. per sq. dm.	Current Efficiency Per cent	*P*-chloro-benzoic acid Yield g.	*P*-chlorotol-uene recov-ered cc.	REMARKS
Yes	None	None	100	4.5	...	...	0.07	14	20 per cent HNO_3 oxidizes *p*-chlorotoluene to *p*-chlorobenzoic acid.
Yes	None	None	100	9	...	...	0.61	13	Same
Yes	None	None	100	18	...	...	1.16	11	Same
Yes	None	None	100	4.5	...	...	1.10	12	25 per cent HNO_3 oxidizes p-chlorotoluene to *p*-chlorobenzoic acid.
Yes	2	2	100	4.5	4	9.5	0.83	12	Very little *p*-chlorobenzoic acid obtained.
Yes	2	2.5	100	4.5	4	33.1	2.97	10.7	Increased yield of *p*-chlorobenzoic acid.
Yes	2	2.5	100	4.5	4	27.4	3.5	10.5	Decreased yield of *p*-chlorobenzoic acid.
Yes	2	2.5	80	4.5	4	23.3	2.11	10.2	Current efficiency less than at 100° C. See Curve on Fig. 7.
Yes	2	2.5	60	4.5	4	3	0.33	13	Same
Yes	2	3	40	4.5	4	None	None	14	Same
Yes	3	3.5	100	3	6	30.8	2.77	11	
Yes	1.0	2	100	9	2	36.4	3.8	10	Increased current efficiency (See Experiment 2).
Yes	0.5	2	100	18	1	42.7	4.9	7	Same
Yes	0.25	1.85	100	18	0.5	64.9	4	8	Same
Yes	0.125	1.85	100	18	0.25	48.9	2.23	11	Decrease of current efficiency.
No	0.25	1.85	100	18	0.5	63	3.92	9	Diaphragm can be dispensed with.
No	0.25	2	100	18	0.5	96	7.5	5	Yield of *p*-chlorobenzoic acid greatly increased.
No	None	None	100	18	None	...	3.3	9	
No	0.25	2	100	18	0.5	67.2	4.10	42	Slight increase of yield *p*-chlorobenzoic acid.

Fig. 7. The current efficiency decreased rapidly with a decrease in temperature; at 60° only a small amount of *p*-chlorobenzoic acid was obtained, while at 40° none was produced.

Still another set of experiments was conducted to study the effect of current density on the reaction. The optimum temperature of 100° C. was used with 20 per cent nitric acid as anolyte and catholyte. Experiments 2, 7, 8, 9, 10 and 11 give the results of these experiments, and in Fig. 8 the results are plotted. The maximum current efficiency of 64.9 per cent was obtained with a current density of 0.5 amp. per sq. dm. At a current density of 0.25 amp. per sq. dm. the current efficiency had decreased to 48.9 per cent and at current densities of over 0.5 amp. per sq. dm. the current efficiency also decreased. In these experiments, the amount of *p*-chlorobenzoic acid obtained in a blank non-electrolytic experiment for the same length of time, was subtracted from the total amount of *p*-chlorobenzoic acid obtained and the current efficiency was calculated from the difference in weight between the blank and the electrolytic experiment.

Experiment No. 12 was conducted without the diaphragm, using 0.5 amp. per sq. dm. current density. The results were almost the same as with the diaphragm, and the diaphragm may, therefore, be dispensed with.

Glacial acetic acid was tried as a solvent, and the results were better than without the solvent. Experiment No. 13 gives the results of an experiment in which a current density of 0.5 amp. per sq. dm. was used with glacial acetic acid as solvent, and 7.5 g. of *p*-chlorobenzoic acid were obtained. A blank non-electrolytic experiment (No. 14) was then carried out under exactly the same conditions, with acetic acid as solvent and it will be noted that in this case the chemical oxidation was also greater than in the case in which the acetic acid was omitted (experiment C).

An increased concentration of *p*-chlorotoluene only slightly increased the yield of *p*-chlorobenzoic acid as shown in experiment No. 15, in which 50 cc. of *p*-chlorotoluene were used in place of 15 cc. as in previous cases.

In the near future the electrolytic oxidation of other substituted toluenes will be reported.

SUMMARY OF PART II.

1. Fifteen experiments have been carried out to study the electrolytic oxidation of *p*-chlorotoluene to *p*-chlorobenzoic acid in nitric acid solution.

2. The optimum conditions found for the electrolytic oxidation of *p*-chlorotoluene to *p*-chlorobenzoic acid are, the use of 20 per cent nitric acid with a current density of 0.5 amp. per sq. dm. and a temperature of 100° C.

3. It has been shown that a diaphragm can be dispensed with in the electrolytic oxidation of *p*-chlorotoluene to *p*-chlorobenzoic acid in nitric acid solution.

4. Acetic acid has a very beneficial effect on the yield of *p*-chlorobenzoic acid, and increased the current efficiency to 96.0 per cent.

DISCUSSION.

W. C. MOORE[11]: Dr. Lowy, in your explanation of this electrolytic action given us on page 89, do you include nitrous acid among the oxides? Nitrous acid is a much more vigorous oxidizing agent than nitric acid, and it is possible that the electrolytic action produces some nitrous acid. I had occasion to look up the oxidizing power of nitrous acid, and came across some very interesting experiments made by Veley, who suspended a polished copper ball in nitric acid which was free from nitrous acid. There was no action whatever, but as soon as the least trace of nitrous acid formed then the action commenced to go vigorously. The explanation is that the ordinary familiar equation for the action of nitric acid on copper is incorrect. It takes place in two stages. If you have a trace of nitrous acid formed, your nitric acid is reduced by a lower oxide of nitrogen to nitrous acid and in that way action proceeds. The first stage is the reduction of nitric acid by an oxide of nitrogen to nitrous acid; and nitrous acid being formed oxidizes your copper to copper oxide, which dissolves in part of nitric acid to form copper nitrate.

ALEX. LOWY: The melting points after one or two purifications, were that of *p*-chlorobenzoic and *p*-nitrobenzoic acids. Now

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whether there was further nitration I do not know, except for the fact that it is difficult to nitrate these compounds in the presence of considerable amount of water and in the absence of dehydrating agents.

C. J. BROCKMAN[12]: In the non-electrolytic experiments, were the platinum electrodes freshly cleaned, or had they been used in previous experiments?

ALEX. LOWY: The non-electrolytic experiments were produced following the electrolytic ones. The purpose in mind was to see whether the non-electrolytic experiments would produce any oxidation. The time factor, the temperature, etc., were all carefully duplicated.

C. J. BROCKMAN: The point I had in mind is, as Dr. Thatcher said, that sometimes the platinum electrodes do not always behave as expected. In case they were not carefully cleaned after being used in the electrolysis, they might have a special catalytic effect in the non-electrolytic experiments, and cause some slight oxidation.

ALEX. LOWY: You will find that a small amount of *p*-chlorotoluene will be oxidized even without the platinum. I thought you meant *p*-nitrotoluene.

C. J. THATCHER[13]: The presence of a trace of nitric acid is not the only thing that will affect the behavior of the electrode; its past history—whether it has been anodically or cathodically polarized—will have a decided influence on the course of the electrolysis. You bear that in mind, do you not, Prof. Lowy?

ALEX. LOWY: Yes, we have used platinum gauze, the type furnished with the Brown electrolytic apparatus. The object was to get thorough agitation, so that the particles of the *p*-nitrotoluene and *p*-chlorotoluene should come in contact with the electrode surface.

C. J. THATCHER: Was it always treated the same before each electrolysis? Did you ever polarize it in the opposite direction before you used it? If you will try that you may find that it makes a great difference, particularly with platinum.

[12] University of Georgia, Athens, Ga.
[13] Chem. Engr. and Electrochemist, New York City.

ALEX. LOWY: We will take that into account, but, of course, at the beginning of every experiment the platinum is cleaned.

C. J. THATCHER: How you clean it and the way you treat it electrolytically is important.

F. C. FRARY[14]: I have noticed in all three of these papers that the organic electrochemists appear to have overlooked one of the most important methods of obtaining information about their experiments. It has been clearly disclosed and its advantages have been utilized by Foerster and his students in their classic work on electrolytic production of *chlorates,* where it is shown that the simultaneous collection of gas from the cells and from an oxy-hydrogen coulometer, together with the analysis of the cell gases, gives not only efficiency in case you do not have side reactions, but if you get side reactions it gives you an exact measure of these side reactions, and often a determination of their character. Collecting gases and analyzing them would often tell more in a week's time than attempts to isolate products and analyze the liquor would tell in many months of work.

ALEX. LOWY: Dr. Frary has done some work along that line. About a year ago we had a paper on the chlorination of benzene.[15] The evolved gases were passed through wash bottles in order to find the amount of the different gases produced.

F. C. FRARY: The way which gives you the most information is to collect simultaneously over a period of a minute or half a minute, and measure the gas from your cell and from a coulometer in series with it; then by analyzing the cell gas you get an instantaneous current efficiency, reduction efficiency and everything else. You get points on curves at intervals of 15 minutes over the whole experiment, and you can tell exactly what a cell is doing over a series of time intervals without having to remove any sample, while if you attempt to collect the total carbon dioxide it will tell you only the total result you got over a wide concentration change in your material being treated, etc., and that tells you very little in comparison with what you get by these regular gas analyses.

COLIN G. FINK[16]: It would be even better to collect the cathode and anode gases separately.

[14] Director of Research, Aluminum Co. of America, New Kensington, Pa.
[15] Trans. Am. Electrochem. Soc., 43, 107 (1923).
[16] Head, Division of Electrochemistry, Columbia Univ., New York City.

F. C. FRARY: Of course, you can collect them separately if you use a diaphragm, but you should never use a diaphragm if you can avoid it. Sometimes you might get an advantage from separate collection, but you have the disadvantage of having to make two gas analyses, and it will take twice as long, consequently you will get readings only half as often.

ALEX. LOWY: That can be easily done if you are working a small cell, but when working with a cell which has five or six openings, as per diagram on page 84, the figures obtained may not be altogether correct for the two or three minutes that the gases are collected from the cell and the coulometer. Of course, theoretically it is possible; practically a number of corrections must be made. The experiment should then be conducted preferably in a thermostat.

C. J. THATCHER: Prof. Frary says "never use a diaphragm if you can avoid it." I think it is avoided too much. A lot of trouble is run into by trying to avoid a *diaphragm*. Where you do not have to, why do you avoid a diaphragm, Prof. Frary?

F. C. FRARY: Because in practice in doing any electrolytic work on a large scale you must, for reasons of economy, run that cell 24 hours a day, seven days in the week, if possible. Now the diaphragm works nicely for four or five hours, maybe the first 24 hours, but in the presence of organic materials, and even of inorganic materials, you usually get a hardening and a decomposition of the diaphragm; frequently you get breakage of the diaphragm. The diaphragms have considerable electrical resistance; you not only get these mechanical troubles, but you get what is usually undesired, a considerable evolution of heat, you get the introduction of impurities and clogging of circulation so that from the plant standpoint a diaphragm is an unmitigated nuisance.

C. J. THATCHER: If you knew that all those facts were no longer true would you modify your opinion? They are no longer true. I know of diaphragms which have been in continuous operation for two years, and their resistance has not changed since the first day. they are not clogged and not broken unless a man drops a monkey wrench on them; and the resistance is hardly any greater than without a diaphragm. That may seem strange, but

it is a fact. It works out that way in our factory. The diaphragms do not increase in resistance, they are not fragile and will not break.

F. C. FRARY: You have a very unusual set of conditions. You happen not to get into tarry by-products.

C. J. THATCHER: I have used it where we do, and the same thing is true. You cannot get solid material in the pores of glass. Now the *electro-filtros* is very much like a piece of glass. It is smooth, it has no pores. I do not know whether you know it, but electro-filtros has no pores, nothing for solid material to get into, and consequently there can be no increase of resistance. Most porous diaphragms, porcelain, for example, have pores in them which clog. I have used electro-filtros in large scale operations in which sulfuric acid was used and where tarry materials formed, but it did not change the resistance of the diaphragm.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 24, 1924, Dr. C. J. Thatcher in the Chair.

ELECTROCHEMICAL OXIDATION OF AROMATIC HYDROCARBONS.[1]

By Fr. Fichter[2].

Abstract.

Anodic oxygen is probably the most energetic of all oxidizing agents. In this paper carefully studied results are given of various methods of securing some degree of control of the oxidation of organic bodies at the anode. Various electrolytes, carriers and the effect of different anodes, and different current densities are discussed. Carefully conducted experiments are presented and many new results shown. Many unnecessary hypotheses are set aside, and a simpler and probably more nearly correct conception of anodic reactions is presented. [A. W. B.]

The American Electrochemical Society, by appointing a special committee on organic electrochemistry, has thereby testified that this branch of our science is of importance and capable of further development.[3] I should like to contribute to this chapter of electrochemistry, and to point out some possible lines along which research may be continued.

Of the two principal reactions which may be applied to organic substances by means of electrolysis, *viz.*, reduction and oxidation, the former has hitherto been strongly favored[4] and developed with great success. Electrochemical oxidation of organic compounds, on the other hand, has occasionally yielded interesting results, and by the aid of catalysts even furnished technically useful methods; but, generally, experiments on oxidation have ended

[1] Manuscript received June 1, 1923.
[2] Basel, Switzerland.
[3] Cf. C. J. Thatcher, Trans. Am. Electrochem. Soc., 36, 337 (1919).
[4] Cf. Raymond Freas, Trans. Am. Electrochem. Soc., 40, 109 (1921).

in sad disappointment[5], owing to the low yields and the intricate course of reaction. Hence the commercial application of electrochemical oxidation to organic chemistry is being looked upon with considerable doubt.

In the following pages, the object is to try to explain the causes of the failures hitherto experienced, and to lay the foundation for a more thorough investigation of electrochemical oxidation[6], starting with the group of aromatic hydrocarbons, and limiting the discussion to the benzene series. I realize that my work is of a preliminary nature, and that all reactions cannot be made to proceed in the direction desired, so as to obtain yields amounting even approximately to the theoretical. In discussing some new aspects, however, I hope to render a service to future research; for wherever a clear and definite scientific basis is lacking no practical useful methods can be established.[7]

I. OXIDATION OF NUCLEAR HYDROGEN ATOMS.

1. Benzene, C_6H_6.

Benzene, the fundamental aromatic hydrocarbon, is highly resistant to purely chemical oxidizing agents; ozone, hydrogen peroxide, and mono-persulfuric acid alone are able to attack it. Oxidation is effected, however, by oxygen evolved at a platinum anode in sulfuric acid solution. Anodic oxygen, according to the experiments of Renard[8], Gattermann and Friedrich[9], and Th. Kempf[10], forms hydroquinone and quinone. While carrying out and testing this reaction, working together with Robert Stocker[11], I also found pyrocatechol as well as substances arising from a breaking up of the benzene nucleus, such as maleic acid and oxalic acid.

This simple instance at once illustrates the manifold difficulties of electrochemical oxidation. The first difficulty is due to the insolubility of benzene in an aqueous electrolyte or an electrically

[5] Cf. Alexander Lowy and Catherine M. Moore, Trans. Am. Electrochem. Soc., 42, 273 (1922).

[6] I deliberately say *electrochemical* and not *electrolytic* oxidation, as I wish to emphasize that with the present cases the organic substance itself is not an electrolyte.

[7] Cf. L'oxydation electrochimique des combinaisons organiques, par Fr. Fichter, Bull. Soc. vaudoise des Sciences naturelles, **51**, 513 (1917).

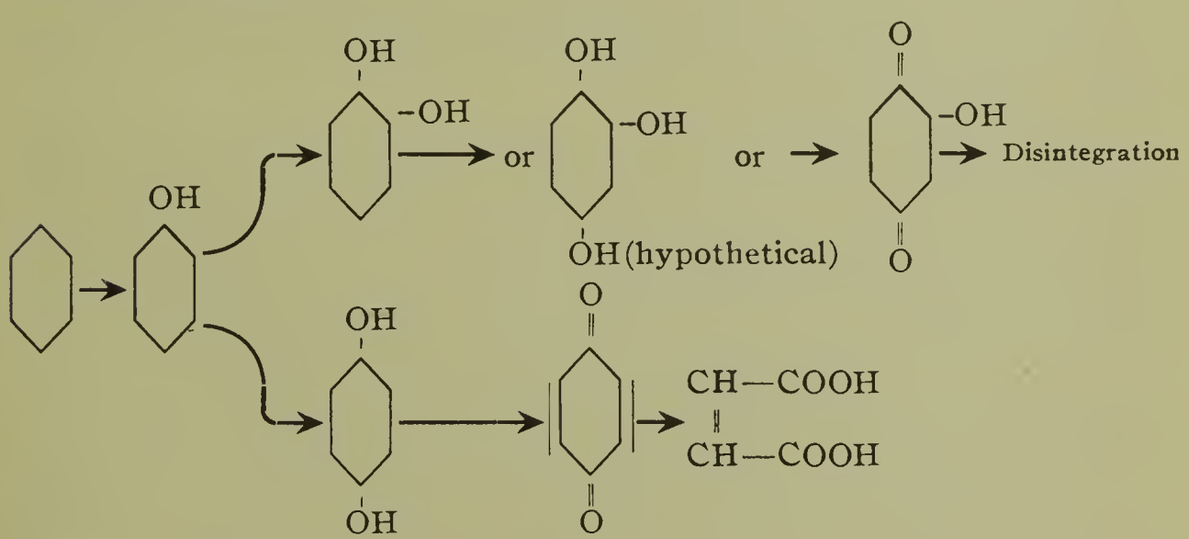
[8] Comptes Rendus de l'Academie des Sciences, Paris, **91**, 175 (1880).

[9] Ber. d. deutsch. chem. Ges. **27**, 1942 (1894).

[10] Th. Kempf, D. R. P. 117251 (1899).

[11] Ber. d. deutsch. chem. Ges. **47**, 2003 (1914).

conducting solvent; vigorous stirring, producing exceedingly fine suspensions or emulsions, makes up only imperfectly for the lack in solubility. We shall presently come across another expedient, the use of solvents which can be mixed with water and with the hydrocarbon, and which at the same time are sufficiently proof against oxidation. I have been disinclined to make use of this expedient in fundamental experiments, because the primary reaction can be distinguished more clearly and unmistakably if every reaction involving the organic solvent is entirely excluded. Now in the case of benzene, on account of its low solubility even in organic solvents, the anode reaction is slow and incomplete. The oxidation products resulting from it, however, dissolve much more readily and, therefore, in their turn undergo a further change long before the benzene has been thoroughly acted on. These conditions are exceedingly unfavorable from an electrochemical point of view. To oxidize benzene a certain oxidation potential is necessary, which could be closely regulated, if there were a definite and sufficient concentration of benzene available as a depolarizer. However, this is not the case, and it is therefore practically impossible to observe the first stage of oxidation of benzene. Probably phenol is first produced,[12] and this then undergoes further oxidation. The process of oxidation may be represented as follows:



the enumerated substances being genetically connected.

Unfortunately there is little prospect of directing the reaction so as to produce an approximately quantitative yield of the signifi-

[12] Perhaps the substance in question is a peroxide-like derivative of phenol.

cant final products, pyrocatechol and quinone. With pyrocatechol this is easily understood, susceptibility to oxidation being its well-known characteristic. But quinone too, which offers such high resistance to purely chemical oxidation, is electrochemically capable of further disintegration, as has been shown by R. Kempf.[13]

These decomposition processes take place the more readily the more the benzene nucleus is saturated with oxygen, and we obtain the not very characteristic final products, oxalic acid, formic acid, carbon monoxide, carbon dioxide. Practically in every electrochemical oxidation of an organic compound, part of the organic compound is oxidized to carbon dioxide and water, because electrolytic oxygen or atomic oxygen, as Bennett and Thompson[14] point out for the parallel case of electrolytic hydrogen, is the most effective oxidizing agent that we possess. This fundamental fact has hitherto not been fully appreciated in investigations on electrochemical oxidation.[15]

2. Means of Moderating the Intensity of Electrolytic Oxidation.

If we wish to obtain fair yields we must retard the violent action of electrolytic oxygen. The most obvious and natural expedient, the increase of the concentration of benzene as a depolarizer, has so far not been possible, as pointed out above.

A second expedient is the regulation of the current density. It is a distinct advantage to keep the anode current density at, or below, 1 amp./sq. dm.

A third expedient lies in the choice of the anode material. Oxidation proceeds most violently at smooth platinum anodes; next to these are peroxidized lead anodes, which we have frequently used. Anodes of graphite and cast magnetite yield practically the same products, but we have not yet thoroughly tried out these anodes, since graphite rapidly disintegrates mechanically and magnetite on account of its low electrical conductivity gives rise to difficulties.

A fourth expedient for checking the violent electrolytic oxidation is the co-operation of the cathode, many investigators having quite unconsciously availed themselves of this means by omitting

[13] J. f. prakt. Chemie (2) **83**, 329 (1911).

[14] Trans. Am. Electrochem. Soc., **29**, 269 (1916); Cf. W. D. Bancroft, Trans. Am. Electrochem. Soc., **37**, 47 (1920).

[15] As a further example of electrolytic oxidation, we might cite the decomposition of amino acids at the anode; cf. Fr. Fichter and Max Schmid, Helv. chim. acta **3**, 704 (1920).

a diaphragm. In the case of benzene, for instance, quinone is kept from further oxidation under these circumstances, owing to the fact that at the cathode it is readily reduced to hydroquinone, this reduction being partial or complete, depending upon the dimensions of the cathode. No stable quinone corresponds to pyrocatechol, therefore it is exposed without protection to the destructive influence of the anodic oxygen, and therefore we always get very moderate yields.

A fifth expedient lies in the careful choice of electrolyte. The most frequent use has hitherto been made of dilute sulfuric acid. K. Elbs[16] suggested that with this electrolyte it was a matter of indirect electrochemical oxidation, inasmuch as sulfuric acid first was oxidized to persulfuric acid, only the latter acting upon the organic substance. I do not consider this hypothesis to be necessary; the oxidation products of benzene in dilute phosphoric acid or perchloric acid, which under the given conditions will not form any peracids, are the same as in the case of sulfuric acid. Very likely also in alkaline solutions the primary products are the same as with sulfuric acid, only here new complications set in owing to the instability of quinone.

A sixth expedient is the use of solutions of salts of metals with several valencies, for example, chromium, manganese, cerium, and vanadium salts. In these cases the metallic ion of higher valency is the real oxidizing agent, for the oxidation of the metal ion at the anode is much more rapidly effected than the oxidation of the aromatic hydrocarbon. We are accordingly dealing with a secondary electrochemical reaction. The use of these multivalent salts seems to be the most promising[17] solution for commercial organic oxidations. I, myself, have not used these multivalent salts to any extent, as I intend to complete first an accurate investigation of primary electrochemical oxidations.

Now it might be argued that the anodic oxidations at platinum anodes, or at lead peroxide anodes, are, properly speaking, also secondary electrochemical reactions, brought about by means of higher oxides. This point is easily tested in the case of lead peroxide anodes, but even if a chemically prepared sample of lead

[16] A. Moser, Elektrolytische Prozesse der organischen Chemie, Halle 1910, p. 66.

[17] Numerous examples will be found in the patent literature; cf. also Alexander Lowy and Elmer H. Haux, Trans. Am. Electrochem. Soc. 40, 123 (1921) and Discussion p. 129.

peroxide, mixed with the organic material in sulfuric solution and heated, should yield products similar to those of a lead peroxide anode, it would not necessarily follow that the electrochemical reaction had been either exhaustively investigated or rendered superfluous. Chemically prepared lead peroxide can, at best, oxidize only with its equilibrium potential; but a lead peroxide anode evolving oxygen has a voltage decidedly higher than the equilibrium potential and therefore acts more vigorously. This oxidation phenomenon can be compared to the parallel behavior of some metals in the case of reductions; the same effect is produced by the evolution of hydrogen by reacting upon the metals with acids and by using the metals as cathodes. Nobody, however, will infer from this parallelism that it is superfluous to study electrochemical reduction at zinc cathodes, on the grounds that it is already known that zinc plus hydrochloric acid will reduce the material under examination.

A seventh expedient is the superimposition of alternating on direct[18] current. With platinum anodes, this method is objectionable on account of excessive corrosion of the electrodes. The method, however, deserves further study.

3. Oxidation of the Phenols.

As to the chemical nature of the oxidation products of benzene by anodic oxygen, it is converted chiefly into compounds of the phenol group.

To study this oxidation more closely, we used phenol as starting material in a number of experiments. Although we could not prove it experimentally, in all likelihood, judging from the process of oxidation, phenol[19] is the first oxidation product of benzene. Owing to the greater solubility of phenol, in aqueous liquors, electrochemical oxidation of phenol proceeds more rapidly than that of benzene.

Thus hydroquinone is obtained as main product with a current efficiency of about 23 per cent, as a maximum, at an anodic current density of 0.25 amp./sq. dm.[20] Pyrocatechol always

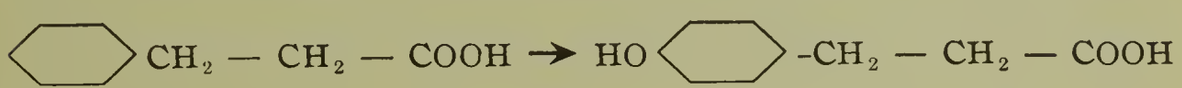
[18] Cf. H. M. Goodwin and M. Knobel, Trans. Am. Electrochem. Soc., **37**, 617 (1920).

[19] This was traced by C. F. Cross, E. J. Bevan and Th. Heiberg besides hydroquinone and pyrocatechol in oxidizing benzene with hydrogen dioxide, Ber. d. deutsch. chem. Ges., **33**, 2015 (1900).

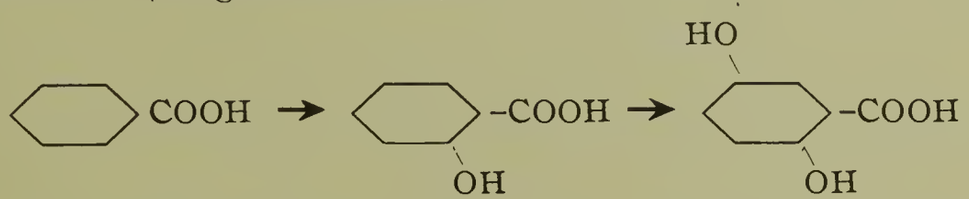
[20] Fichter and Franz Ackermann, Helv. chim acta, **2**, 591 (1919). Still lower current densities do not allow the process of oxidation its full scope, whereas higher densities lead more and more to a complete destruction.

appears in such small quantities that, although it can be identified by the typical color reaction with ferric chloride, and by being precipitated with lead acetate, its quantitative determination yields no trustworthy values. Owing to its greater depolarizing power, pyrocatechol can never appear in higher concentration in presence of hydroquinone. When subjected to further oxidation, pyrocatechol (much like quinone) finally has its nucleus disrupted and fumaric acid is formed; or, if anode and cathode without diaphragm work together, succinic acid. As to the original exact proportion of hydroquinone and pyrocatechol, no definite statement can be made at present; it is not unlikely that they are both produced in about the same amount, or even that pyrocatechol forms the chief product, as in the case of pure chemical oxidation with hydrogen peroxide.

The formation of phenol, pyrocatechol and hydroquinone are all due to the same fundamental reaction; the anodic oxygen introduces hydroxyl groups into the benzene nucleus. This has long been known in electrochemical literature, although the great prevalence of the reaction has not been sufficiently taken into account. Only a thorough investigation, covering the different benzene derivatives, will be able to shed full light on this matter. Regarding the research recently carried out, I should like to present here a few examples only: The oxidation of hydrocinnamic acid in sulfuric acid solution at lead peroxide anodes results in para-hydroxy-hydrocinnamic acid or para-hydrocoumaric acid[21]:



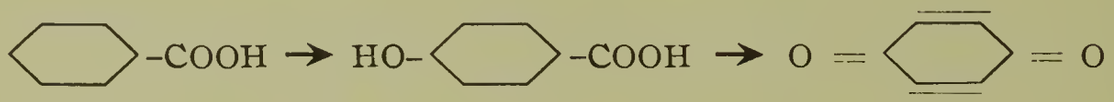
Benzoic acid with high current density at a platinum anode is oxidized to 2.5-dihydroxybenzoic acid[22] = hydroquinone carboxylic acid (or gentisic acid):



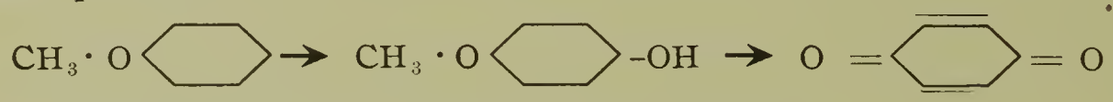
If the product resulting from the introduction of hydroxyl groups is in any way convertible into a para-quinone, the forma-

[21] Rudolf Senti, unpublished experiments.
[22] Fr. Fichter and Eldor Uhl, Helv. chim. acta, 3, 22 (1920).

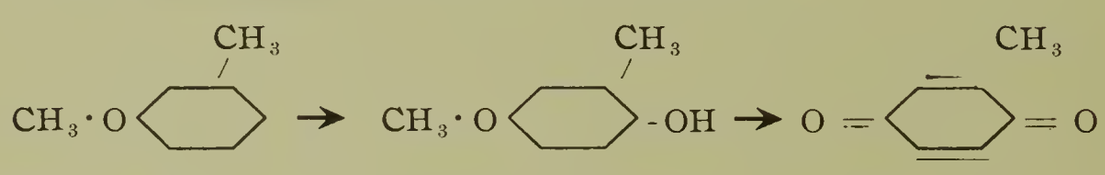
tion of para-quinone always takes place, without regard to any opposing side groups, which are simply ejected. Thus among the oxidation products of benzoic acid, besides hydroquinone carboxylic acid, also hydroquinone may be found, *i. e.*, in reality quinone which at the cathode has simply been converted into hydroquinone, and which is derived from para-hydroxybenzoic acid, with the elimination of the carboxyl group.



The formation of quinone is even more readily effected with anisole and similar phenolic ethers[23], since the methoxy-group very strongly increases the reactivity of the hydrogen atom in the para-position:

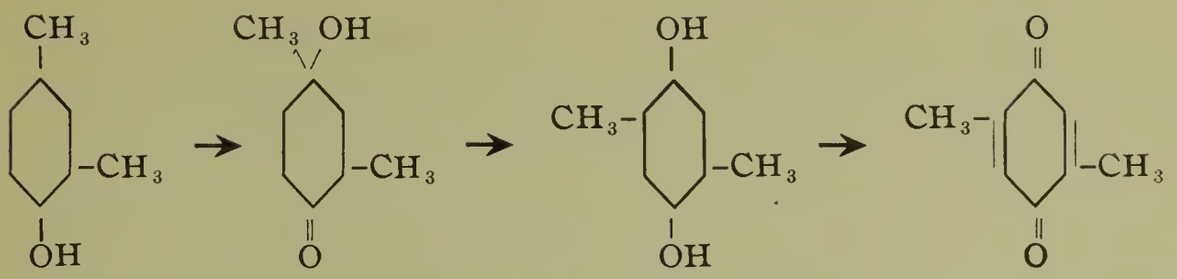


or, in the case of methyl ether of meta cresol[24]



The most interesting reaction of this kind which we have observed is that of meta-xylene[25]. We found para-xyloquinone among the oxidation products of meta-xylene. We were first inclined to attribute its formation to the presence of para-xylene, which is almost inevitably present even in the purest meta-xylene obtainable. To decide the matter definitely, we prepared absolutely pure xylenol (partly *via* meta-xylene sulfonic acid, partly *via* carefully purified meta-xylidine), and then obtained, under suitable conditions, a much more complete formation of para-xyloquinone. For meta-xylenol (which probably results from meta-xylene as the first oxidation product) is oxidized to a certain type of quinones known as 2.4-dimethylquinole, discovered by E. Bamberger and F. Brady.[26] This itself cannot be isolated, owing to its being rearranged by the sulfuric acid to para-xylohydroquinone and oxidized by the current to para-xyloquinone:

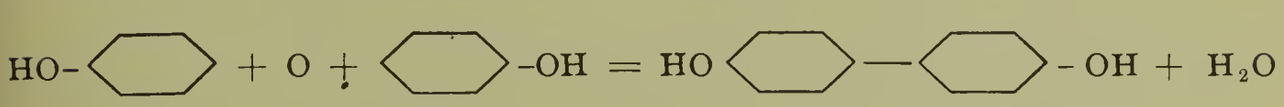
[23] Willy Dietrich, Helv. chim. acta, **7**, 131 (1924).
[24] Heinrich Ris, unpublished experiments.
[25] Jacques Meyer, unpublished experiments.
[26] Ber. d. deutsch. chem. Ges., **33**, 3642 (1900).



Accordingly, starting out from meta-xylene, on account of the strong anodic oxidation, we obtain directly a para-xylene derivative. The correctness of these conclusions we proved by oxidizing pure meta-xylidine according to the method of Noelting and Th. Baumann[27] using chromic acid and obtaining merely toluquinone; then substituting with bromine the meta-xylenol derived from the above meta-xylidine and obtaining tribromoxylenol, (melting point, 179° C.) with a yield of 95 per cent; and this same meta-xylenol on electrochemical oxidation gave para-xyloquinone, with the surprisingly high yield of 28 per cent.

4. The Nuclear Linkage.

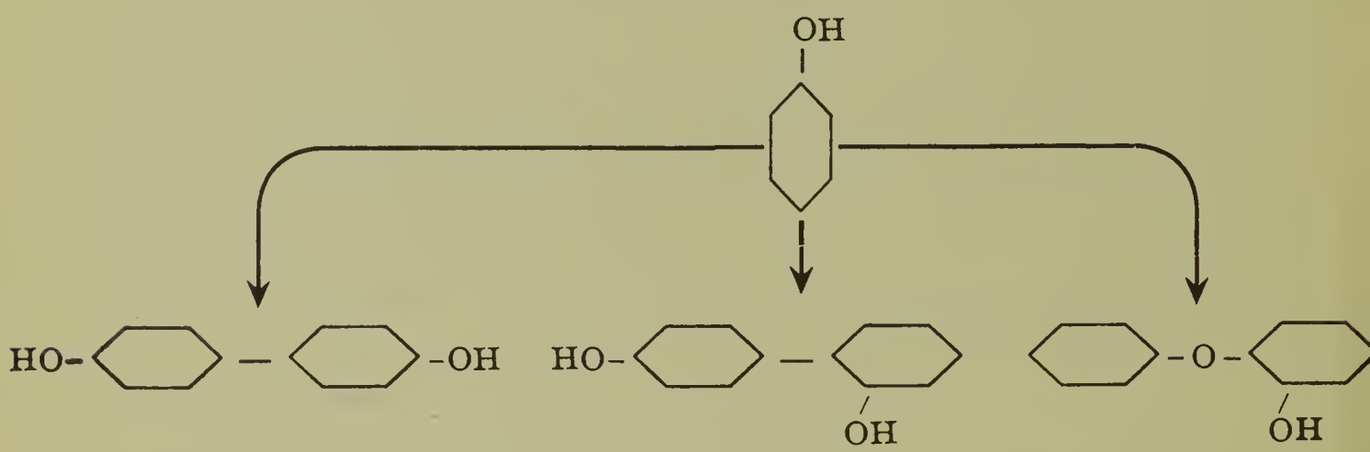
Besides bringing about the introduction of hydroxyl groups (into ortho- and para-positions) the electrochemical oxidation of phenols may give rise to nuclear linkage, such as the formation of diphenyl derivatives. The first case of this kind dates far back, but at the time it was not properly understood, since fundamental facts were lacking. When E. Drechsel[28], on trying to imitate biochemical reactions by means of alternating current electrolysis, electrolyzed phenol in a weakly acid sulfate solution, using platinum electrodes, he obtained, among many other products, di-para-oxy-di-phenyl. Its formation can only be accounted for by supposing that the oxidizing phase of the alternating current attacked the organic compound and that the oxidation product thus formed was not reduced back again to the original material by the reducing wave of the current[29]:



By systematically investigating this reaction, we[30] oxidized a great excess of phenol, employing lead peroxide anodes and a low cur-

[27] Ber. d. deutsch. chem. Ges., **18**, 1151 (1885).
[28] Journal f. prakt. Chem., (2) **29**, 229 (1884); **31**, 135 (1886); **38**, 65 (1888).
[29] Fr. Fichter and Robert Stocker, Ber. d. deutsch. chem. Ges., **47**, 2003 (1914).
[30] Fr. Fichter and Emile Brunner, Bull. Soc. chim. de France (4) **19**, 281 (1916).

rent density (0.25 amp./sq. dm.); we thus obtained, besides pyrocatechol and hydroquinone, more than three other compounds, the formation of which must be explained by nuclear linkage. The three compounds so far established are di-para-oxydiphenyl, ortho-para-dioxydiphenyl, and ortho-hydroxy-diphenole ether[31], in which latter the linkage of the two nuclei is brought about by a bond of oxygen:

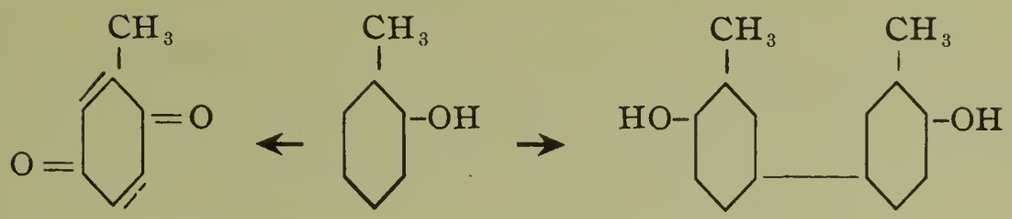


It appears safe to assume that these compounds are intermediate products in the formation of hydroquinone and pyrocatechol; di-para-oxydiphenyl, upon further oxidation would produce two molecules of quinone and ortho-para-dioxydiphenyl one molecule of quinone, and one molecule of pyrocatechol. Indeed the diphenols, which first separate out in a resin-like layer, disappear again upon continuing the oxidation or upon increasing the current density.

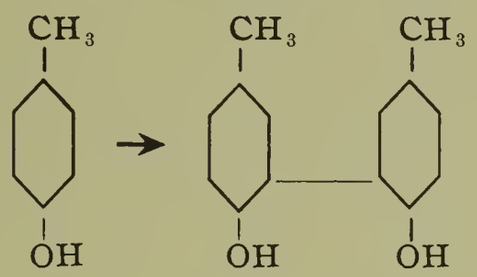
The ortho-hydroxy-diphenole ether is a dehydration product of pyrocatechol and phenol; it is formed at the anode, splitting off water, a reaction which has been frequently observed, but as yet is not thoroughly understood.

The nuclear linkage is even more pronounced with the phenol homologues, for as soon as the smooth formation of para-quinone is counteracted, owing to the nucleus being filled, the diphenyl derivatives are formed more abundantly. Thus ortho-cresol[32] gives toluquinone on the one hand and on the other ortho-dicresol

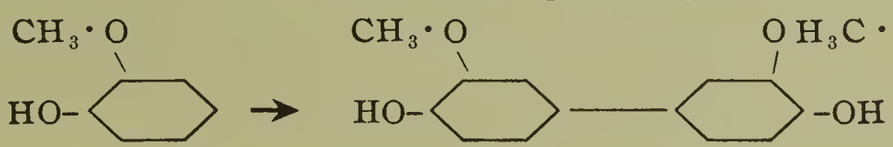
[31] Cf. F. Ullmann and A. Steiner, Ber. d. deutsch. chem. Ges. 39, 622 (1906).
[32] Fr. Fichter and Fr. Ackermann, Helv. chim. acta, 2, 583 (1919).



whereas para-cresol yields chiefly para-dicresol

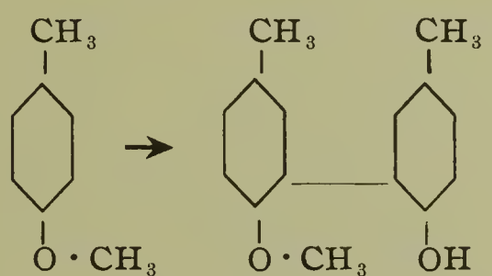


Guaiacol[33], under suitable conditions, gives diguaiacol

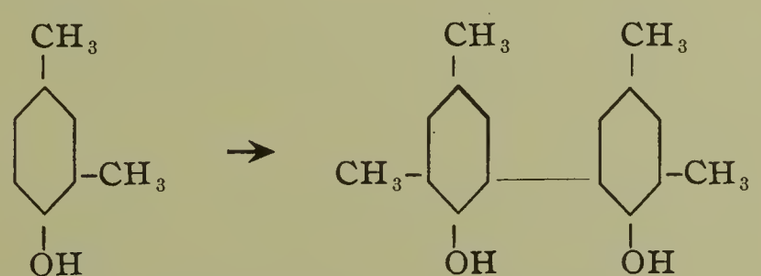


Veratrol, when submitted to electrochemical oxidation behaves similarly.

From the methylic ether of para-cresol[34], we obtain the monomethylic ether of para-dicresol, through partial elimination of methyl.



Irrespective of the above described rearrangement into paraxyloquinone, meta-xylenol[35] is electrolytically oxidized to dixylenol, when oxidation is not too energetic, with a yield amounting to 33 per cent. Through chemical oxidation dixylenol is very difficult to obtain.



[33] Willy Dietrich, Helv. chim. acta, **7**, 131 (1924).
[34] Heinrich Ris, unpublished experiments.
[35] Jacques Meyer, unpublished experiments.

However, I should not like to give the impression that the reactions, which appear to be so simple from the above formulæ, actually proceed smoothly in every case and result in substantial yields. This must not be expected, in view of the fact that oxidations of this kind are only possible by means of very strong oxidizing agents, and invariably there is some destructive decomposition. On the other hand, anodic oxygen shows no partiality and will react with two or more nuclei which offer themselves for linkage. The derivatives of diphenyl are all volatile *in vacuo* at a moderately elevated temperature, and therefore they are easily purified. But besides these we also generally find phenol-like substances of higher molecular weight, frequently in large quantities which boil only at extremely elevated temperatures and show little tendency to crystallize. We have not yet succeeded in isolating these in a pure state.

5. *Azobenzene.*

It may appear presumptuous to cite only those investigations which were carried out in my own laboratory, but I can easily explain this. In going over older published statements I have found time and time again that our organic electrochemical literature is teeming with errors, partly due to misconceptions and partly due to incorrect observations. For example, according to the literature the two oxidizing reactions which we have been discussing above, *viz.*, the introduction of hydroxyl groups into the nucleus, and the nuclear linkage are not only observed in the case of benzene and its homologues, the phenols, phenolic ethers, and carboxyl acids, but also in the case of many other benzene derivatives. A paper covering this subject, choosing azobenzene as a starting material, has been in existence for years, but it failed completely to recognize the facts.

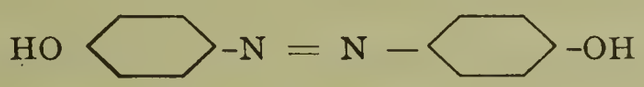
Heilpern[36] had stated that azobenzene subjected to oxidation in concentrated sulfuric acid was converted into tetraoxy-azobenzene, with good yields:

$$C_6H_5 \cdot N = N \cdot C_6H_5 \rightarrow C_6H_3(OH)_2N = NC_6H_3(OH)_2$$

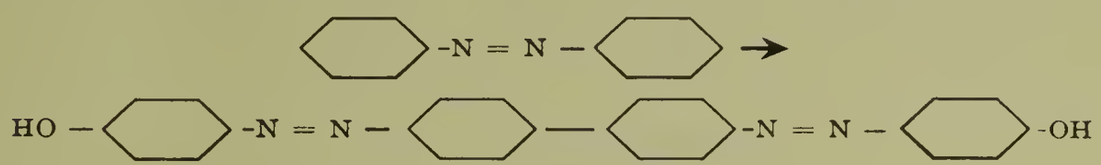
Together with W. Jaeck[37], I repeated this experiment. There is

[36] Z. f. Elektrochem., 4, 89 (1897).
[37] Helv. chim. acta, 4, 1000 (1921).

no smooth reaction; the products are of a complex nature, but do not include the compound mentioned by Heilpern. We have so far been able to isolate and identify positively two substances, para-dihydroxy-azobenzene (or para-azophenol)

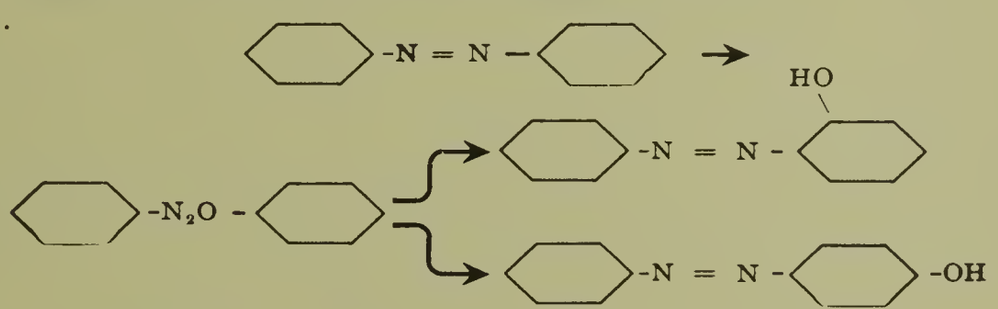


and diphenyl-disazo-phenol



Besides these two there are present in large quantities, substances of high molecular weight and of low solubility.

Heilpern is right only insofar as we are actually dealing with an introduction of hydroxyl groups. This reaction, to all appearances, however, does not take a direct course, but avails itself of the azo-group for the introduction of the oxygen. At first probably azoxybenzene is produced which in concentrated sulfuric acid is rearranged to para- and ortho-oxyazobenzene:



The further oxidation of para-oxyazobenzene to the two final products para-dihydroxy-azo-benzene and diphenyl-disazo-phenol is easily understood. What becomes of the ortho-oxyazobenzene we have not been able to find out. It is likely subjected to a far-reaching decomposition: phenol and acetic acid can be detected without difficulty in every experiment.

Heilpern's report is an example of the extraordinarily superficial manner in which research in the sphere of electrochemical oxidation of organic substances is frequently carried out. The fundamental mistake of older workers was to attach miraculous powers to anodic oxygen; it was supposed, for example, readily to convert aromatic bases to technically useful dyestuffs. Heilpern

believed he produced such a dye, probably on account of diphenyl-diazo-phenol behaving as a direct dye. Long before Heilpern, Friedrich Goppelsroeder had similarly tried to obtain aniline dyes directly by electrochemical oxidation, but in spite of his many varied experiments no commercial process resulted.[38]

The patent literature abounds in incorrect statements as to the smooth course of certain electrochemical oxidations. All this has made me skeptical, and accordingly I have confined myself in this paper to those reactions which I have personally investigated.

II. OXIDATION OF THE SIDE-CHAIN.

6. Toluene.

H. D. Law and F. Mollwo Perkin[39] studied the electrochemical oxidation of the benzene homologues. In one experiment they used as much as 4 kilograms of toluene, in suspension in dilute sulfuric acid, and oxidized it at a platinum anode, but they obtained only carbonic acid gas and water. After that they invariably used mixtures of toluene, acetone and dilute sulfuric acid, and thus succeeded in obtaining benzaldehyde, although the yields were small (13 to 14 per cent)[40]. Analyzing their first unsuccessful experiments, we are bound to arrive at the following conclusion: the platinum anode in dilute sulfuric acid is such a powerful oxidizing agent that it will entirely decompose toluene, unless checked in some way. Acetone moderates the intensity of the oxidation, due, no doubt, to the fact that the solubility of toluene and hence its concentration as a depolarizer is increased; secondly, the first oxidation products, such as benzyl alcohol, which are more soluble in water and which without the intervening acetone would be unprotectedly exposed to the anode, are now able to take refuge with the toluene in the acetone layer; thirdly, acetone by itself is subject to anodic oxidation and thus to have a depolarizing effect.

In the past a fundamental error has been made in interpreting the above results. Since anodic oxygen converts toluene into benzaldehyde and, on the other hand, dilute nitric acid oxidizes

[38] Cf. Fr. Fichter, Friedrich Goppelsroeder, Verh. d. Naturforsch. Ges. Basel, **31**, 133 (1920) with extensive bibliographical references.

[39] Trans. Faraday Soc. **1**, 31 (1904).

[40] F. Mollwo Perkin, Practical Methods of Electrochemistry, London, 1905, p. 279.

toluene to benzoic acid, therefore it was thought that oxygen evolved at a platinum anode is a weaker oxidizing agent than nitric or chromic acid. This reasoning is entirely wrong.

Anodic oxygen being the most powerful oxidizing agent, it must be compared with the strongest chemical oxidizing agents only. H. D. Law and F. M. Perkin[41] actually found that lead dioxide, manganese dioxide, persulfate and chromyl-chloride act analogously to anodic oxygen, yielding directly aldehydes and not acids. Text-books calmly pass over this striking parallelism.

Anodic oxygen was considered to be a weak oxidizing agent, because in the final product only aldehydes are to be found, and not the corresponding acids. Nobody will doubt that the oxidation of toluene takes place by a gradual introduction of oxygen, which may be represented as follows:

$$C_6H_5 \cdot CH_3 \rightarrow C_6H_5 \cdot CH_2 \cdot OH \rightarrow C_6H_5 : CHO \rightarrow$$
$$C_6H_5 \cdot COOH \rightarrow C_6H_4(OH) \cdot COOH \rightarrow C_6H_3(OH)_2 \cdot COOH \rightarrow \ldots$$

We should expect benzoic acid as a final product, provided that benzaldehyde were oxidized at the anode just up to the stage of benzoic acid, without further complications. All this was taken for granted and in no way tested experimentally.

However, if an attempt is made to oxidize, quantitatively, benzaldehyde to benzoic acid at the anode, it is surprising[42] to find invariably a shortage of about 25 per cent. This is due to the fact that benzoic acid is further oxidized at a platinum anode to hydroquinone carbonic acid and quinone and ultimately is completely decomposed to carbon dioxide and water.

Benzaldehyde, instead of acting as an anodic depolarizer and preventing further oxidation, on the contrary increases the oxidation potential, evidently through the formation of a superoxide-like derivative, the presence of which is easily shown by potential measurements. It is not the assumed inactivity of anodic oxygen, but, on the contrary, the intense activity of this oxygen which causes the benzaldehyde to appear as final product. The benzaldehyde, owing to its insolubility in water, is far better protected than benzoic acid.

[41] J. Chem. Soc. (London) **91**, 258 (1907).
[42] Fr. Fichter and Eldor Uhl, Helv. chim. acta, **3**, 22 (1920).

7. *Para-Nitrotoluene.*

What holds true for toluene likewise holds for para-nitrotoluene. K. Elbs[43] discovered the exceedingly interesting and significant fact that it is oxidized in glacial acetic acid at platinum anodes to para-nitrobenzyl alcohol. This is again not an evidence of "weakness" on the part of anodic oxygen but, on the contrary, of strength. For, first, it is known that the nitrotoluenes are much less readily attacked by chemical oxidizing agents than toluene itself; secondly, the para-nitrobenzyl alcohol is by no means obtained in a quantitative amount; thirdly, there is, in fact, also formed some aldehyde[44] and, with an excess of current, a slight quantity of the acid, which perhaps escaped the observation of Elbs; and fourthly, an attempt at further oxidizing the alcohol electrochemically[45] results in a far-reaching decomposition, with a simultaneous formation of nitric acid, the presence of which, especially in aqueous solution, usually promotes the oxidative destruction of the organic substances at the anode. In choosing glacial acetic acid as a solvent, Elbs made an exceedingly good choice; glacial acetic acid keeps back the destructive effect of nitric acid, and therefore acts as a protector for the alcohol. But para-nitrobenzyl alcohol is not the chief oxidation product because it is incapable of further oxidation at the anode, but because a further oxidation chiefly attacks the nucleus and thus, in completely destroying the molecule, produces only insignificant "wrecks."

It is important to bear in mind that in the living organism para-nitrotoluene is also oxidized to para-nitrobenzyl alcohol[46]. Biochemical oxidations are frequently violent; they too, apart from yielding characteristic products, always result in a complete decomposition down to carbon dioxide and water. A certain resemblance between the processes of electrochemical and biochemical oxidation undoubtedly exists; it has repeatedly led to the view that living organisms oxidize by electrochemical means.[47] However, this is probably going too far and the resemblance is prob-

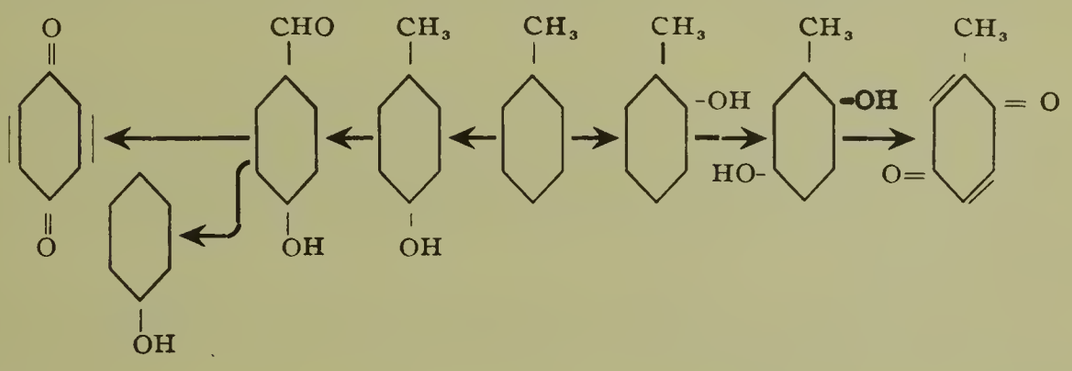
[43] Z. f. Elektrochem., 2, 522 (1896).
[44] Labhardt and Zschoche, Z. f. Elektrochem., 8, 93 (1902).
[45] Fr. Fichter and Gérald Bonhôte, Helv. chim. acta, 3, 395 (1920).
[46] M. Jaffé, Z. f. physiolog. Chem. 2, 47 (1878-79).
[47] Cf. Fr. Fichter, Z. f. Elektrochem., 27, 487 (1921).

ably merely due to the fact that anodic oxygen and biochemically vitalized oxygen are both energetic oxidizing agents of a similar "potential."

8. Oxidation of Toluene in the Nucleus.

The first investigators of the anodic oxidation of toluene were primarily only concerned with the fate of the side-chain, since nitric acid and chromic acid, the chemical oxidizing agents generally used, affect the side-chain only; but apart from the aldehyde, as F. M. Perkins[48] previously observed, other substances, to which organic chemists apply that all-embracing term "resins," were formed but not further examined.

R. Stocker and myself[49] observed that toluene was by no means oxidized in the side-chain only, but, as might be expected, simultanoeusly oxidized also in the nucleus. We worked without acetone and moderated the violence of oxidation by an excess of toluene and a low anodic current density. Thus we managed to trace toluquinone, quinone and phenol, during the formation of which the following intermediate stages were passed:



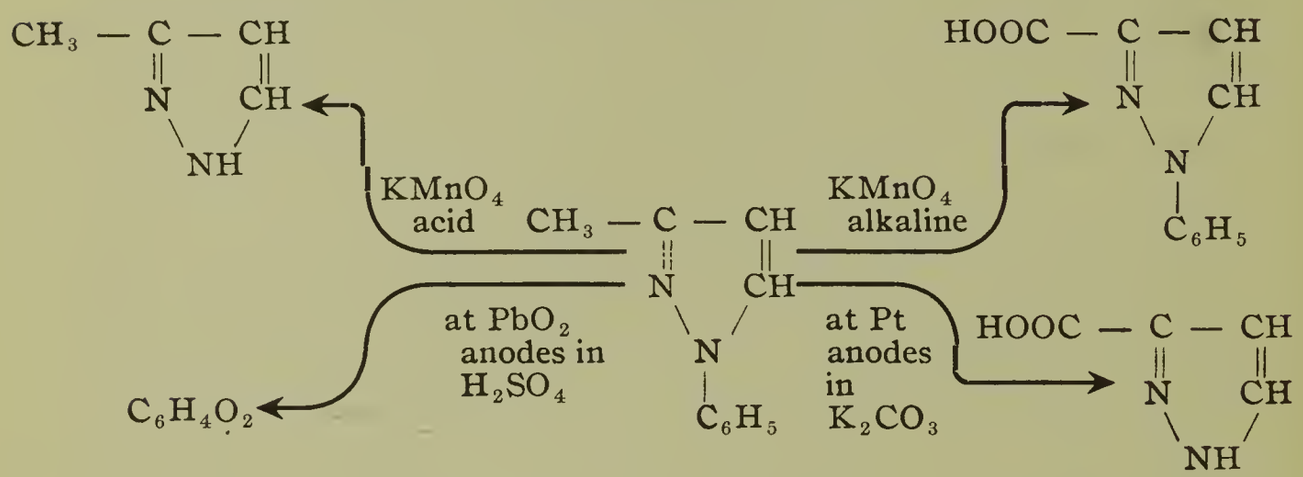
This we corroborated by directly investigating the oxidation of ortho- and para-cresol.

In the above scheme neither the oxidation to benzaldehyde is considered, nor the formation of dicresols and pyrocatechol-like dioxytoluenes, which, when treated with ferrichloride, reveal their presence by strong color reactions.

We see from this example that the electrochemical oxidation of benzene homologues proceeds by various routes, diverging fan-like and resulting in a large diversity of products. The problem of disentangling and characterizing these products requires fre-

[48] Practical Methods, p. 280, "a considerable quantity of a resinous substance."
[49] Ber. d. deutsch. chem. Ges., **47**, 2017 (1914).

quent repetition of the experiments under varying conditions. But the task is attractive from a scientific point of view, for the extraordinary power of anodic oxygen may lead to results hitherto unknown. To illustrate our contention we cite an experiment with one of the pyrazole series. The oxidation products of 1-phenyl-3-methyl-pyrazole, obtained either by means of potassium permanganate or by anodic oxidation[50], we consider as:



Here again the anodic oxygen proves to be far more energetic as an oxidizing agent.

9. Oxidation of the Side-Chain of other Substituted Toluenes.

There are two questions which present themselves:

1. Is it possible to direct the attack either on the nucleus or on the side-chain?

2. Is it possible to modify the attack on the side-chain by substitution in the nucleus?

The effect of directing the oxygen to the side-chain is of course attained by replacing the hydrogen atoms of the nucleus. As the introduction of hydroxyl groups takes place, as far as we have hitherto observed, chiefly in the para- and ortho-position to the methyl groups, toluenes substituted in para- and ortho-position are of special interest.

J. Sebor[51] oxidized para-toluene sulfonic acid at lead dioxide anodes to para-sulfo-benzoic acid with a yield of as much as 34 per cent. G. Grisard[52] and I were surprised to find that the

[50] Fr. Fichter and Hugues de Montmollin, Helv. chim. acta, **5**, 256 (1922).
[51] Z. f. Elektrochem., **9**, 371 (1903).
[52] Helv. chim. acta, **4**, 928 (1921).

cyanogen group had a still more favorable effect, since para-tolunitrile in a mixture of acetone and sulfuric acid (its solubility in water is too small) is oxidized at lead dioxide anodes to para-cyano-benzoic acid, with a material yield of 37 per cent; simultaneously terephthalic acid was produced giving a material yield of 7.5 per cent. The reaction is similar with meta-tolunitrile giving a 28 per cent yield of meta-cyano-benzoic acid; on the other hand, ortho-tolunitrile was strongly decomposed. The effect of the cyanogen group is here especially marked by the fact that it is not the aldehyde but the acid which is formed, perhaps due to the fact that the formation of peroxides does not take place at the aldehyde stage.

At our laboratory we are at present about to examine carefully the effects of different substituents upon the oxidation of the side-chain of toluene.

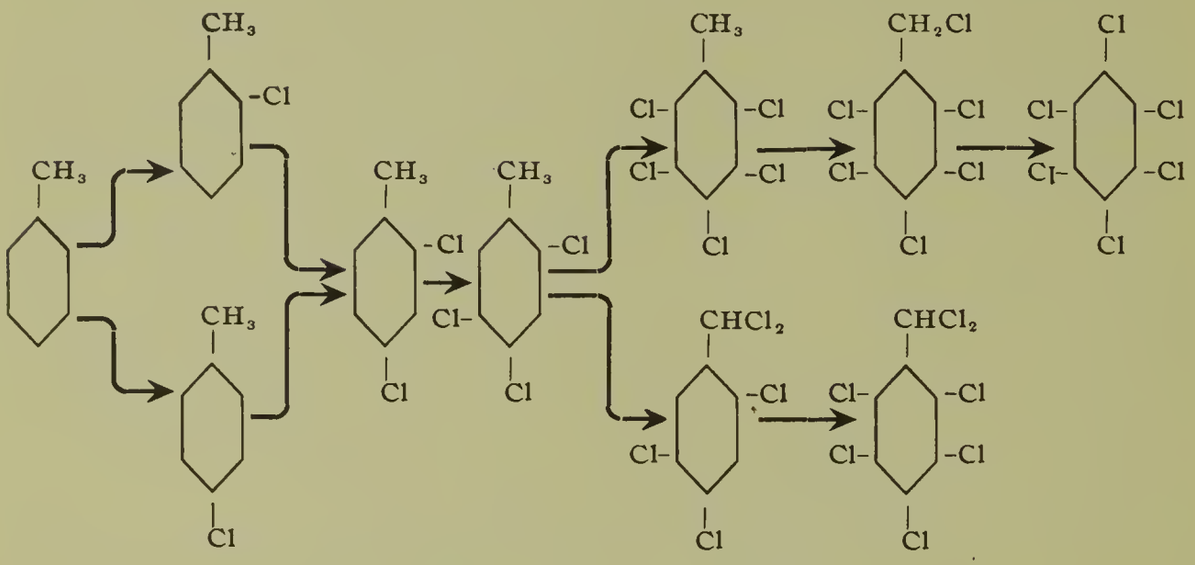
ELECTROCHEMICAL CHLORINATION OF TOLUENE.

If we oxidize toluene electrochemically in sulfuric suspension, the introduction of hydroxyl groups in place of the hydrogen atoms of the nucleus is the chief reaction. This is similar to the electrochemical chlorination of toluene.

This classical example shows that the substitution may be arbitrarily directed to the nucleus or to the side-chain if carried out by chemical methods, according to the conditions chosen (halogen in the presence of carriers at low temperatures or halogen without carriers at high temperatures in the presence of light.). If carried out electrochemically, only the nucleus is attacked at first, as Lupu Glantzstein and myself[53] discovered when employing a homogeneous solution of toluene in a mixture of glacial acetic acid and concentrated hydrochloric acid. Upon excluding light, to prevent secondary reactions on the part of the liberated unreacted chlorine on the side-chain, and with a gradually increased current density up to 1 amp./sq. dm. we finally obtained trichlortoluene, with the sole participation of the nuclear hydrogen atoms; only at higher current densities does the side-chain join in, the resulting final products being hexachlorobenzene on the one hand, and on

[53] Ber. d. deutsch. chem. Ges., 49, 2473 (1916).

the other an oxygenated compound, penta-chlore-tolu-hydroquinone.

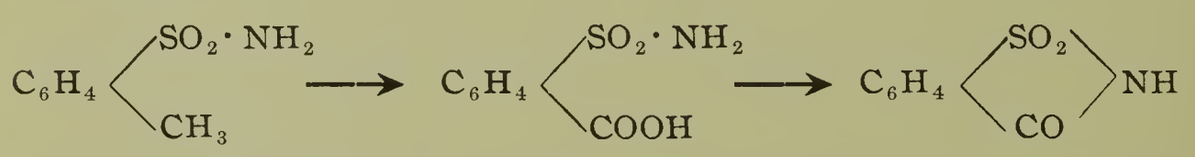


Electrochemical chlorine is as energetic a chlorinating agent as electrochemical oxygen is an energetic oxidizing agent; without using carriers, with sufficiently high current density, the nucleus is fully substituted. Anodic chlorine, exactly like anodic oxygen, favors the hydrogen atoms of the nucleus.

11. Electrochemical Synthesis of Saccharine.

Now if the problem is given to counteract the natural propensity of anodic oxygen and to leave the nucleus unacted upon, and oxidize the side-chain to carboxyle, then it is necessary to take good care to study every effect of the anode material, the current density, the composition of the electrolyte, etc. We can actually select suitable conditions, as I should like to show in the case of the synthesis of saccharine.

For the electrochemical oxidation of ortho-toluene-sulfon-amide to saccharine



there exists, aside from methods employing catalysts, a "method" patented by F. von Heyden's successor[54], according to which ortho-toluene-sulfonamide, in the presence of an excess of caustic soda is oxidized to saccharine. This statement is wholly unten-

[54] D. R. P. 85491 (21. IV. 1895), expired 1901.

able, at least so far as anodes of platinum, nickel or copper are concerned. Mere traces of saccharine are formed; the main portion of the product is lost through combustion. Hans Löwe and I[55] found that the electrochemical oxygen first attacks the amido-group, and then the benzene nucleus, which is indicated by the solution turning a brown color. An ammoniacal electrolyte diverts the oxygen from the amido-group to the methyl-group. A similar effect is obtained in a warm double-normal sodium carbonate solution. To moderate the oxidation, a lead dioxide anode would be preferable to a platinum anode; but lead dioxide is dissolved in an alkaline liquid. If, on the other hand, a platinum anode is combined with a lead cathode, omitting diaphragms, a small quantity of lead dissolves at the cathode as sodium plumbite which, at the platinum anode, forms a thin layer of lead dioxide and this regulates the oxidation. The oxidation of the methyl group to carboxyle is insured by the alkaline electrolyte; according to the Cannizzaro reaction, the aldehyde is continuously decomposed to acid and alcohol. Thus it is possible to promote the formation of saccharine up to a yield of 75 per cent, without any discoloration of the electrolyte taking place.[56]

CONCLUSION.

In conclusion, I may have furnished little that is new, and perhaps I have not even managed to remove the impression that the only purpose of electrochemical oxidation is to break up organic compounds. It will certainly require most energetic research to plow through the vast domain. Should I in the present paper have succeeded in giving a fresh impulse to investigators, I shall have attained my object. I am convinced that if anodic oxygen is regarded and employed in its proper sense, namely, as the most efficient of all oxidizing agents, it will lead to many new results, some of which may be of commercial importance.

DISCUSSION.

ALEX. LOWY[55]: On page 107, fifth line from the bottom, "the former has hitherto been strongly favored and developed with

[55] Helv. chim. acta, 5, 60 (1922).
[56] Hans Löwe, Brit. Patent 174913 (5 I. 1922), Swiss Priority (31.I.1921)
[55] Prof. of Organic Chemistry, Univ. of Pittsburgh, Pittsburgh, Pa.

great success," and the second line from the bottom, "by the aid of catalysts even furnished technically useful methods." I would like to have more specific information pertaining to those two statements.

A. W. BURWELL[56]: The electrolytic oxidation of toluol and of naphthalin as well as of anthracene has been carried out in this country in commercial plants. At least two of these bodies have been so oxidized in Europe. But in all cases catalytic agents have been used, so it may be claimed that the products were not made by direct electrolytic oxidation. As for reduction products, I believe Dr. Fichter refers to the production of paramidophenol and of anilin both from nitrobenzol. In these two cases no catalytic agents are used, wherefore the processes may be truly called electrolytic reductions.

C. J. THATCHER[57]: On the second point, Prof. Lowy, all that we are doing now commercially is, one might say, by the aid of catalysts; that is, considering chromium compounds as catalysts. They pick up oxygen from the electrode and carry it to the anthracene or the toluene which we wish to oxidize. I think that was what Prof. Fichter had in mind.

A. W. BURWELL: In part, that is true. In my own work with chromic salts I have made many thousands of pounds of phthalic acid and thousands of pounds of benzoic acid. I have found it expeditious to separate the electrolytic oxidation of the chromic salts to chromic acid from the oxidation of the organic body. Control is better, therefore, yields are better; it is easier to handle the solutions and to recover the product. The cells are simpler in construction. Cheaper labor may be used.

In the case of oxidations in the cell proper, constant conditions are more easily maintained. However, these conditions can be closely approached outside of the cell. Proper concentrations of the carrier must be arrived at and maintained. This is different for each body to be oxidized. For good commercial yields the available oxygen for the oxidation of toluol must not be higher than 0.31 per cent, nor must it go below 0.16 per cent. Above the higher figure yields are low due to too vigorous reaction, and

[56] Consulting Chemist, Jersey City, N. J.
[57] Chem. Engr. and Electrochemist, New York City.

below the lower figure the temperature must be held too high with the same result. There is a range for each body to be oxidized. With very few exceptions it is necessary to have present a large excess of the starting material to protect the desired product from further oxidation. Temperature is just as important a factor.

C. J. THATCHER: I note that Prof. Fichter on pages 110 and 111, in enumerating the various means of moderating the intensity of electrolytic oxidations, did not include that very method which Dr. Burwell spoke about just now, namely, dissolving benzoic acid in toluol, or dissolving hydroquinone in benzol. That works well in practice particularly if you have a constant flow of toluol or benzol from your cell. That keeps the concentration of the end product low. Prof. Fichter apparently overlooked that.

A. W. BURWELL: This point has never been stressed in any of the papers. To get high electrolytic efficiency in the production of chromic acid there must always be an excess of chromic sulfate present.

C. J. THATCHER: Prof. Fichter seems to wish to emphasize the fact that, as he states in his conclusion, "anodic oxygen should be employed in its proper sense, namely, as the most efficient of all oxidizing agents." That is what Prof. Fichter has attempted to bring out. We should consider, as Dr. Burwell said, that electrolytic processes are largely electrochemical; that is, in oxidation it is the oxygen that is chemically oxidizing (or an oxygen derivative) and in reduction it is hydrogen or a derivative.

HENRY ARNSTEIN[58]: I wish to say that we have conducted successful experiments for the *electrolytic oxidation of alcohol.* We had in view producing commercially pure acetic acid, free of the usual impurities always found in acetic acid when produced by the dry distillation of wood. In our experiments we were obtaining acetic acid of about 60 to 65 per cent strength. These experiments are still in progress. As to our experiments on the production of ether, we are manufacturing this and using it in connection with alcohol as a motor fuel. Since the present automobile engine was built for low compression, it is difficult to

[58] Consulting Chemist, Philadelphia, Pa.

start this engine with pure alcohol as a fuel. To overcome this difficulty we dehydrate about 25 per cent of the alcohol and this etherized alcohol then makes an excellent fuel. There are at present two plants in the course of construction where the electrolytic oxidation of alcohol will be carried out, one in California, and one in Colombia, South America.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 24, 1924, Dr. C. J. Thatcher in the Chair.

THE FUNCTION OF PEROXIDES AND PERACIDS IN THE ELECTROCHEMICAL OXIDATION OF ORGANIC COMPOUNDS.[1]

By Fr. Fichter.[2]

Abstract.

Kolbe's hydrocarbon synthesis appears to be primarily an oxidation reaction. Numerous Kolbe reactions are discussed in detail. In many cases platinum anodes at high current densities are essential to bring about the reaction. The oxidation potential of elemental fluorine is equal to or greater than that of nascent oxygen. The peroxide-formation hypothesis has many advantages over other hypotheses.

In 1891 Alex. Crum Brown and James Walker[3] suggested that the formation of ethane, as discovered by Hermann Kolbe[4] during the electrolysis of alkali acetates, should be considered an ionic reaction. According to their view, the acid anions set free at the anode are the unstable intermediate products which subsequently yield ethane, or methyl acetate, or, in the case of propionic acid, ethylene.

I. Experiments do not substantiate this explanation of Kolbe's synthesis.

If the above theory is correct we would expect Kolbe's reaction to take place the more readily, the greater the dissociation of the salt used. The author and Th. Lichtenhahn[5] tried to carry out Kolbe's synthesis with the salts of the strong sulfo-aliphatic

[1] Manuscript received January 14, 1924.
[2] Universität, Basel, Switzerland.
[3] Ann. d. Chemie, **261**, 107 (1891).
[4] Ann. d. Chemie, **69**, 257 (1849).
[5] Z. f. Elektrochem., **20**, 471 (1914); Ber. d. deutsch. chem. Ges., **48**, 1949 (1915).

acids, but met with great disappointment. Ammonium sulfo-acetate, $NH_4.OOC.CH_2.SO_3.NH_4$, yielded a limited amount of the expected synthetic derivative, that is, ethylene disulfonic acid,

$$\begin{array}{l} NH_4.O_3S.CH_2.COO' \\ NH_4.O_3S.CH_2.COO' \end{array} = \begin{array}{l} CO_2 \\ CO_2 \end{array} + \begin{array}{l} NH_4.O_3S - CH_2 \\ \quad\quad\quad\quad\quad\quad | \\ NH_4.O_3S - CH_2 \end{array}$$

and in addition, a small quantity of methane disulfonic acid. No trace of synthetic products could be found in the case of potassium β-sulfo-propionate $KOOC.CH_2.CH_2.SO_3K$. Ethylene only was formed, and the decomposition by oxidation (as in the case of sulfo-acetic acid) destroyed the main portion of the material.

This unexpected failure led to a critical investigation of Kolbe's hydrocarbon synthesis, as applicable to the aliphatic series. Since Kolbe's discovery, another and entirely different theory from that explaining the reaction by discharged anions has repeatedly been advanced. According to this other view, it is an oxidation proper with which we are dealing. By way of introduction, and in order to establish this hypothesis, I wish to express an opinion which may afford a lucid explanation of many electrochemical reactions.

II. THE ELECTROCHEMICAL OXIDATION OF ORGANIC COMPOUNDS IS NOT MYSTERIOUS.

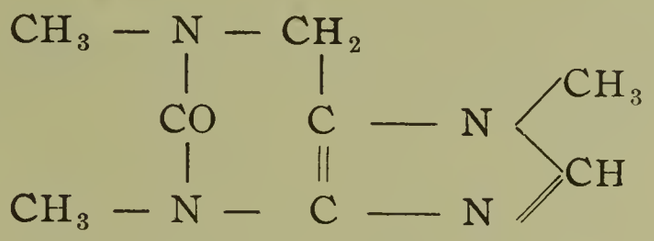
A veil of mystery has hitherto been frequently cast upon electrochemical oxidations and reductions in inorganic and organic chemistry. There are a number of compounds which were first produced by electrolysis, and which will, for practical purposes, always be produced electrolytically. However, with reference to the action of oxygen and hydrogen, it is shown by the potential tables of oxidation and reduction agents, and the tables of anodic and cathodic overvoltages, at the different electrodes, that with the right potential we can produce any effect of oxidation or reduction, regardless of whether this potential is attained by means of electrical voltage or by certain chemical reagents. The principle that every electrochemical reaction can be imitated chemically, and that, inversely, it is possible to enforce any chemical reaction by electrochemical means, does not in the least affect the quantitative results; and just in this respect the

electrochemical procedure in many cases deserves preference. A thorough study of these phenomena will only tend to emphasize this fact.

Two examples will illustrate the above principle, the first from the sphere of electrochemical reductions; the second from that of electrochemical oxidations.

III. CAFFEINE CAN BE REDUCED BY PURELY CHEMICAL MEANS.

Julius Tafel in studying the electrochemical reduction of the acid amides[6] and the acid imides[7] discovered the class of desoxyxanthines, of which desoxycaffeine[8] is an example:



Up to the present time our literature has generally considered this fine hydrogenation a specific electrochemical reaction. It was by this method that Tafel[9] succeeded in reducing uric acid to purone; whereas Emil Fischer[10] found no reaction of sodium amalgam on uric acid even after several months. However, the reduction potential which Tafel maintained at pure lead cathodes in acid solution was comparatively high. Accordingly, W. Kern[11] experimented with purely chemical methods and succeeded in easily reducing caffeine to desoxycaffeine, with the aid of zinc dust.

IV. A BISULFATE CAN BE CONVERTED INTO A PERSULFATE BY OTHER THAN ELECTROLYTIC MEANS.

Erich Müller[12] showed that by adding a fluoride to the electrolyte the yield of persulfate could be appreciably increased. Similar observations have been made with respect to other electrochemical

[6] J. Tafel and Th. B. Baillie, Ber. d. deutsch. chem. Ges., **32**, 68 (1899).

[7] J. Tafel and M. Stern, Ber. d. deutsch. chem. Ges., **33**, 2224, (1900).

[8] Th. B. Baillie and J. Tafel, Ber. d. deutsch. chem. Ges., **32**, 3206 (1899); C. F. Boehringer Söhne, D.R.P. 108577, Dec. 29, 1898.

[9] J. Tafel, Ber. d. deutsch. chem. Ges., **34**, 238 (1901).

[10] Ber. d. deutsch. chem. Ges., **17**, 329 (1884).

[11] Unpublished experiments.

[12] Z. f. Elektrochem., **10**, 776 (1904).

anodic reactions. The author and Jakob Müller[13] also found fluorides to be almost indispensable for the electrolytic formation of perphosphates, which previously had only been prepared by purely chemical methods.[14] It must be admitted that A. Rius y Miro[15] later on discovered proper conditions of alkalinity which lead to the formation of potassium perphosphate, $K_4P_2O_8$, without any addition of fluoride. However, good yields, permitting the isolation of solid potassium perphosphate, can be obtained only in the presence of potassium fluoride.

It seems easy to explain the favorable result of the addition of fluoride on the direct action of the fluorine developed at the anode. This opinion was expressed some time ago by F. W. Skirrow.[16] Owing to the improved methods of preparing fluorine, due to the investigations of W. L. Argo, F. C. Mathers, B. Humiston and C. O. Anderson[17], the author and K. Humpert[18] were at last enabled to test the usefulness of the above theory by allowing elementary fluorine to act directly upon a potassium bisulfate solution. We actually obtained potassium persulfate, which evidently is produced according to the equation:

$$2KHSO_4 + F_2 = K_2S_2O_8 + 2HF.$$

The introduction of fluorine results, after several hours, in the crystallization of almost pure persulfate. Fr. Foerster in his excellent book on "Elektrochemie wässriger Lösungen"[19] says: "The oxidation of sulfuric acid and its salts to the persulfuric acid (discovered by M. Berthelot) and persulfates is, in the presence of water, possible only by means of electrolysis." This statement has lost its validity; the oxidation potential of elemental fluorine approaches or surpasses that of ozonized oxygen developed at platinum anodes, and therefore is sufficient for the oxidation of bisulfate to persulfate.

Having shown that neither the reduction of xanthines to desoxyxanthines, nor the oxidation of bisulfates to persulfates is

[13] Helv. chim. acta, **1**, 297 (1918).
[14] J. Schmidlin and P. Massini, Ber. d. deutsch. chem. Ges., **43**, 1162 (1910).
[15] Helv. chim. acta, **2**, 3 (1919).
[16] Z. f. anorg. Chem., **33**, 25 (1903).
[17] Journ. phys. Chem., **23**, 348 (1919); Trans. Am. Electrochem. Soc. **35**, 335 (1919); cf. also F. Meyer and W. Sandow, Ber. d. deutsch. chem. Ges., **54**, 759 (1921).
[18] Helv. chim. acta, **6**, 640 (1923).
[19] Third Edition (1922), p. 836.

a specifically electrochemical reaction, the undeniable fact remains that the preparation of desoxycaffeine, or of potassium persulfate, can be carried out in an exceedingly convenient way by means of electrolysis.

V. PEROXIDES ARE INTERMEDIATE PRODUCTS OF KOLBE'S SYNTHESIS.

Let us now return to Kolbe's electrochemical hydrocarbon synthesis. By treating acetic anhydride with barium superoxide, P. Schützenberger[20] obtained ethane and carbon dioxide. From J. Brodie's[21] experiments we know, however, that acetic anhydride in ethereal solution is oxidized by barium peroxide to acetyl peroxide, $CH_3.COO.OOC.CH_3$. Thus the formation of ethane and carbon dioxide by the electrolysis seems to be the result of the decomposition of acetyl peroxide, an intermediate product:

$$\begin{array}{lcll} CH_3 - COO & & CH_3 & CO_2 \\ \quad\quad\quad\; | & = & \;| & + \\ CH_3 - COO & & CH_3 & CO_2 \end{array}$$

The formation of the acetyl peroxide itself would have to be attributed to the powerful oxidizing action of a platinum anode with a high current density.[22] The acetate or the acetic acid liberated at the anode directly produces the high oxygen-bearing but unstable acetyl peroxide. Accordingly, it is easy to understand why platinum anodes and high current densities are indispensable for Kolbe's hydrocarbon synthesis.

The idea that during the electrolysis of acetate the formation of acid peroxides as intermediate products takes place has, apart from earlier authors, been expressed most clearly by C. Schall[23], who compared the phenomenon with the electrochemical conversion of dithiocarbonic acids into supersulfides at the anode.[24] The validity of this hypothesis may be tested by preparing pure acetyl peroxide[25] and then causing it to decompose. However, this experiment,

[20] Comptes Rendus de l'Acad. des Sciences, Paris, **61**, 487 (1868).

[21] Jahresber. über die Fortschritte der Chemie, 317 (1863).

[22] Fr. Fichter and Eduard Krummenacher, Helv. chim. acta, **1**, 146 (1918).

[23] Z. f. Elektrochemie, **3**, 83 (1896).

[24] Cf. also the possibility of the intermediate formation of a peroxide as considered by Fr. Foerster and A. Piguet in connection with potential measurements. Fr. Foerster and A. Piguet, Z. f. Elektrochem., **10**, 729 (1904); furthermore G. Preuner and E. B. Ludlam, Z. f. physik. Chem., **59**, 689 (1907).

[25] Preferably by following A. M. Clover and C. F. Richmond, Am. Chem. J., **29**, 179 (1903).

which is rather dangerous owing to the violence of the explosion, never leads to an absolutely unquestionable result; it always yields methane besides ethane.[26] The temperature of the exploding substance is so high that the decomposition reactions, due to a kind of cracking process, obscure the normal development, and consequently methane, which is stable at the highest temperature, predominates more and more.

Again it is preferable to conduct the reaction not by purely chemical but by electrochemical means, on account of the smooth course of the latter method, which comprises a series of intimately connected processes.

The formation of the acetyl peroxide at the anode can be interpreted in different ways. One way is to assume that the discharged acetate anions immediately combine to form acetyl peroxide,

$$\begin{matrix} CH_3 - COO' \\ \\ CH_3 - COO' \end{matrix} + 2 \oplus = \begin{matrix} CH_3 - COO \\ \quad | \\ CH_3 - COO \end{matrix}$$

A second assumption attributes the formation of acetyl peroxide to the evolution of anodic oxygen. The latter view seems more plausible as the invariably observed oxidation of acetic acid to the end products, carbon dioxide and water, is traced to the same cause as the synthesis of ethane.

VI. WORKING ANODES MAY CAUSE SPLITTING OFF OF WATER.

Now, a new difficulty arises, inasmuch as by purely chemical methods the peroxides of the aliphatic acids have so far always been produced from the anhydrides by the aid of such vigorous oxidizing agents as barium peroxide, sodium peroxide, or hydrogen peroxide; in other words, not by a de-hydrogenation of acetic acid, but by the introduction of oxygen into acetic acid anhydride:

not $$\begin{matrix} CH_3 - COOH \\ \\ CH_3 - COOH \end{matrix} + O = \begin{matrix} CH_3.COO \\ \quad | \\ CH_3.COO \end{matrix} + H_2O$$

but $$\begin{matrix} CH_3.CO \\ \diagdown \\ \quad O \\ \diagup \\ CH_3.CO \end{matrix} + O = \begin{matrix} CH_3.COO \\ \quad | \\ CH_3.COO \end{matrix}$$

[26] Fr. Fichter, Z. f. Elektrochem., **20**, 473 (1914); Fr. Fichter and Eduard Krummenacher, Helv. chim. acta, **1**, 152 (1918).

The question then is, May we suppose that at a platinum anode in acetate solutions there is a temporary formation of acetic acid anhydride? A dehydrating action has often been observed at the anode, which may be illustrated by the following remarkable example:[27]

A mixture of 100 cc. of a saturated solution of ordinary ammonium carbonate and 5 cc. of ethyl alcohol was electrolyzed in a platinum vessel, which served as anode; a little spiral tube of lead served as cathode. About 10 amp. hr. were used in the electrolysis, after which the solution was evaporated to dryness, leaving a mixture of ammonium nitrate and acetamidine nitrate,

$$CH_3 \cdot C\begin{matrix}\diagup NH_2 \\ \diagdown\!\!\diagdown NH\end{matrix} \cdot HNO_3$$

Upon repeatedly evaporating with barium carbonate the ammonium nitrate is decomposed, whereupon the acetamidine nitrate[28] can be separated from the barium nitrate by alcohol. The alcohol is oxidized at the platinum anode to aldehyde; the latter takes up ammonia and forms aldehyde ammonia, which in turn is oxidized to acetamide. It is impossible by purely chemical means, with the aid of aqueous ammonia, to substitute the imide group for oxygen in the acetamide. With liquefied ammonia, when heated in a sealed tube, in the presence of ammonium nitrate (which is necessary for the preservation of the acetamidine formed) there results a moderate yield of acetamidine nitrate:

$$CH_3 - C\begin{matrix}\diagup NH_2 \\ \diagdown\!\!\diagdown O\end{matrix} + H_2NH = H_2O + CH_3 - C\begin{matrix}\diagup NH_2 \\ \diagdown\!\!\diagdown NH\end{matrix}$$

The acetamidine nitrate is again isolated by evaporation with barium carbonate, and as it is the salt of a stronger base it remains unattacked. So we see that, in aqueous solution, there is a splitting off of water at the anode. If not effected in an electrochemical way, it would be necessary that water be totally excluded beforehand. This proves that the intermediate formation of acetic anhydride undoubtedly is possible.

[27] Z. f. Elektrochem., **18**, 652 (1912); Fr. Fichter, C. Stutz and Fr. Grieshaber, Verh. d. Naturf. Ges. Basel, **23**, 253 (1912).

[28] The nitric acid of the nitrates obtained is due to the oxidation of the ammonium carbonate, cf. Fr. Fichter and Hans Kappeler, Z. f. Elektrochem., **15**, 937 (1909).

Without further discussing the special problem of the antecedent of the acetyl peroxide, which we can not yet entirely solve, we will now turn to the more important question, How is the acetyl peroxide decomposed at the anode? Why does the decomposition proceed in such a regular way without formation of any methane and without formation of carbon, which always results through the explosion of chemically prepared acetyl peroxide?

VII. AT THE WORKING ANODE THE TEMPERATURE IS HIGHER.

The electrolytic process has the invaluable advantage that the acetyl peroxide never collects in any considerable quantity, but as soon as it is formed it is decomposed, the latter step taking place without developing any excessively high temperature. There are two reasons for this: The nature of the anode, and the temperature of the anode surface.

Platinum as anode metal decomposes peroxides catalytically; this is such a well-known phenomenon (for example with finely-divided platinum black and hydrogen peroxide) that no further discussion is necessary. It is out of the question that a considerable amount of acetyl peroxide should collect in contact with the platinum of the anode.

The temperature of an anode in an electrolyte which is subject to oxidation always exceeds the temperature of the surrounding solution; for instance, in the electrolysis of acetate, the oxidation of acetic acid to its end products takes place in such a way that the heat due to the combustion of the acetic acid is given up at the anode. This must lead directly to a local increase of temperature at the anode surface, which is more than sufficient to decompose the acetyl peroxide.

The preparation of urea by means of electrolyzing a concentrated solution of ammonium carbonate may serve to prove the correctness of the view taken above. As is well known, this reaction was discovered by E. Drechsel[29], who employed alternating current or quickly commutated direct current. He thought the result to be due specifically to alternating current. We, however, easily managed to show that the formation of urea takes place exclusively at the anode, and that much better yields are obtained

[29] J. f. prakt. Chem., (2) 22, 476 (1880).

with direct than with alternating current. Nevertheless, it is impossible to think of any equation representing the oxidation of ammonium carbonate to urea, since these two substances differ only with regard to their percentage of water.

However, urea is not the only product formed at the anode in solutions of ammonium carbonate; on the contrary, its formation is far less marked than that of the oxidation of ammonia, and the heat, generated by the formation of nitrate of ammonia from ammonia and oxygen, is set free at the anode. By calculating the amount of heat from the quantity of nitrate found, it can be ascertained to what temperature the solution at the anode was heated. In a direct test, a measured volume of an ammonium carbonate solution, of the same concentration and the same percentage of free ammonia, as in the electrolysis above, was brought to the desired temperature in a sealed tube and gave yields of urea much like those obtained electrolytically. Thus, Drechsel's urea synthesis is, in truth, not an electrochemical, but rather an electrothermic reaction, due to the conversion of strong solutions of ammonium carbonate into urea by local heating at the anode.[30] The reaction can also be effected by strong chemical oxidizing agents, like calcium permanganate, hydrogen peroxide, or ozone.

VIII. CAN THE DECOMPOSITION OF PEROXIDES BE CONTROLLED?

Direct attempts at decomposition of acetyl peroxide did not lead to a simple disintegration according to the equation

$$\begin{array}{lcll} CH_3 - COO & & CH_3 & CO_2 \\ \quad\quad\quad\; | & \rightarrow & \; | & + \\ CH_3 - COO & & CH_3 & CO_2 \end{array}$$

Decomposition is rendered complicated by formation of methane at high temperatures. In spite of this weakness in the argument, Emil Baur[31], judging from experiments with commutated direct current, recently arrived at the conclusion that acetyl peroxide was to be regarded as an unstable intermediate product in the electrolysis of acetates.

The failure in the case of acetyl peroxide must be attributed

[30] Fr. Fichter, H. Steiger and Th. Stanisch, Verh. d. Naturf. Ges. Basel, 28, II, 66 (1917); Fr. Fichter, Z. f. Elekrochem., 24, 41 (1918).

[31] Z. f. Elektrochem., 29, 105 (1923).

to the violence of the explosion. As the size of the molecule of the peroxide increases, the velocity of decomposition decreases, and the high temperature secondary reactions disappear. Speaking of propionyl peroxide, A. M. Clover remarks:[32] "When heated to 80°, a slow effervescence takes place and continues until the decomposition is complete. Hydrocarbons and carbon dioxide are evolved . . ." By careful heating (60°) in a small flask, we actually managed[33] to conduct the decomposition of propionyl peroxide so carefully that the gases could be collected over mercury. Under these conditions there invariably occurred also the formation of methane due to cracking, and accordingly a non-volatile amorphous residue of lower hydrogenous compounds; but we regularly obtained the normal products of reaction, that is, butane and carbon dioxide, according to

$$\begin{array}{lll} CH_3 - CH_2 - COO & & CH_3 - CH_2 \quad CO_2 \\ & \rightarrow & \quad\quad | \quad + \\ CH_3 - CH_2 - COO & & CH_3 - CH_2 \quad CO_2 \end{array}$$

The escaping gaseous mixture contained 58.4 per cent CO_2, 16.9 per cent C_4H_{10} and 24.7 per cent CH_4; the ratio of CO_2 and C_4H_{10} is 3.46:1, instead of 2:1. Besides that, a small quantity of ethyl propionate, $CH_3.CH_2.COO.CH_2.CH_3$, could be detected, which is also formed in the electrolysis of the propionates.

Succinates electrolyzed yield ethylene and carbon dioxide, according to A. Kekulé's[34] investigations. To explain this reaction it must also be assumed that a peroxide is first formed, which then is simply decomposed according to

$$\begin{array}{lll} CH_2 - COO & & CH_2 \quad CO_2 \\ | \quad\quad | & = & \| \quad + \\ CH_2 - COO & & CH_2 \quad CO_2 \end{array}$$

To verify this equation A. Fritsch[35] and I prepared the amorphous succinyl peroxide, following the directions of L. Vanino and E. Thiele.[36] Succinyl peroxide may be decomposed preferably by heating it in xylene with a reflux-cooler; CO_2 and C_2H_4

[32] Thesis, Univ. of Michigan, Ann Arbor, 1914, p. 10.
[33] Fr. Fichter and Eduard Krummenacher, Helv. chim. acta, 1, 153 (1918).
[34] Ann. d. Chemie, 131, 79 (1864).
[35] Helv. chim. acta, 6, 329 (1923).
[36] Ber. d. deutsch. chem. Ges., 29, 1724 (1896).

are formed in a volume ratio of 2.25:1 (instead of 2:1). It may be noted also that in the electrolysis of the succinates the theoretical volume ratio is not readily obtained; we found in one such experiment 2.4 vol. CO_2 to 1 vol. C_2H_4.

A. M. Clover and A. C. Houghton[37] in a quite similar way decomposed the demilateral succinic peroxide, which they discovered, and obtained adipic acid besides carbon dioxide:

$$\begin{array}{l} HOOC - CH_2.CH_2.COO \\ \qquad\qquad\qquad\quad | \rightarrow \\ HOOC - CH_2.CH_2.COO \end{array} \quad \begin{array}{l} HOOC.CH_2.CH_2 \\ \qquad\qquad\quad | \\ HOOC.CH_2.CH_2 \end{array} \quad \begin{array}{l} CO_2 \\ + \\ CO_2 \end{array}$$

Accordingly, A. Crum Brown and J. Walker's[38] interesting electrochemical synthesis of adipic acid, by electrolysis of the potassium salt of the acid succinic ester, can also be easily explained by assuming the intermediate formation of an, as yet unknown, ester peroxide, according to the reactions:

$$\begin{array}{l} ROOC.CH_2.CH_2.COOH \\ \qquad\qquad\quad \rightarrow \\ ROOC.CH_2.CH_2.COOH \end{array} \quad \begin{array}{l} ROOC.CH_2.CH_2.COO \\ \qquad\qquad\qquad\quad | \rightarrow \\ ROOC.CH_2.CH_2.COO \end{array} \quad \begin{array}{l} ROOC.CH_2.CH_2 \\ \qquad\qquad\quad | \\ ROOC.CH_2.CH_2 \end{array} \quad \begin{array}{l} CO_2 \\ + \\ CO_2 \end{array}$$

After the experiments with succinyl peroxide we tried fumaryl peroxide. In this case also the point was to find a rational explanation for one of the oldest electrolyses[39] of salts of organic acids. Fumaryl peroxide[40], when heated in a little steel bomb, breaks up into acetylene and carbon dioxide according to the equation:

$$\begin{array}{l} CH - COO \\ \quad\| \qquad\quad | \\ CH - COO \end{array} = \begin{array}{l} CH \\ \quad\| \\ CH \end{array} + \begin{array}{l} CO_2 \\ \\ CO_2 \end{array}$$

It must be admitted that the yield of acetylene was only 15.7 per cent of the quantity calculated from the volume of carbon dioxide; on the other hand, by electrolysis we obtained only 19.9 per cent of the calculated amount of acetylene.[41]

[37] Am. Chem. J., **32**, 43 (1903).

[38] Ann. d. Chem., **261**, 107 (1891).

[39] A. Kekulé, Ann. d. Chem., **131**, 88 (1864).

[40] L. Vanino and E. Thiele, Ber. d. deutsch. chem. Ges., **29**, 1726 (1896).

[41] In connection with these experiments compare also the interesting decomposition of silver glutarate by iodine, probably through the intermediate stage of glutaric acid peroxide. A. Windaus, F. Klänhardt and G. Referey, Ber. d. deutsch. chem. Ges., **55**, 3981 (1922).

To explain Kolbe's synthesis as being due to the discharged acid anions is inapplicable in the case of benzoic acid. Yet a benzoate is dissociated in the same manner as an acetate, and just as discharged acetate anions give ethane and carbon dioxide, so discharged benzoate anions would have to yield diphenyl and carbon dioxide. Attempts have been made to prepare diphenyl synthetically from benzoates by electrolysis in aqueous solution, but they all failed. Not until quite recently did C. Schall[42] accomplish the electrochemical synthesis of diphenyl by excluding water and employing a solution of manganese benzoate in *fused* benzoic acid.

In general, the first reaction at the platinum anode is the formation of a peroxide; such an intense oxidation at the carboxyl group, however, is possible only if the hydrocarbon radicle of the organic acid is resistant to oxidation. This assumption by no means applies to benzoic acid, which, at platinum anodes, even in acid solution, is vigorously attacked, and hydroxyl groups are introduced into the benzene nucleus; thus the product formed is hydroquinone carbonic acid[43], which, however, in turn partly decomposes by oxidation. The basic requirement for Kolbe's synthesis, that is, the stability of the hydrocarbon radicle against oxidation, is fulfilled only in comparatively few groups of organic acids. This easily accounts for the fact that the reaction is limited really to the saturated mono- and dibasic aliphatic acids. Many assertions to the contrary, found in our literature, are erroneous. Thus Lilienfeld[44] held that he obtained at the anode ethylene diamine from the copper salt of glycocoll, an opinion which was supported by Kühling.[45] This is an illusion; at the anode glycocoll undergoes a fargoing decomposition, the nascent formaldehyde condenses with the liberated ammonia forming a mixture of mono-, di- and tri-methylamine, which those observers took for ethylene diamine.[46]

Now, since we know that in Kolbe's synthesis acid peroxides are formed as intermediate products, we can perform the same synthesis without electrolysis, as was shown above, provided that

[42] Z. f. Elektrochem., 28, 506 (1922).
[43] Fr. Fichter and Eldor Uhl, Helv. chim. acta, 3, 22 (1920).
[44] D. R. P. 147,943 (1903).
[45] Ber. d. deutsch. chem. Ges., 38, 1638 (1901).
[46] Fr. Fichter and Max Schmid, Helv. chim. acta, 3, 704 (1920).

we succeed in obtaining a preparation of the acid peroxide itself. This is exceedingly simple in the case of benzoyl peroxide[47], which is easily prepared in a pure state. After being heated to 180-200° for a short time in a steel bomb it decomposes rapidly into carbon dioxide and diphenyl[48]:

$$\begin{matrix} C_6H_5.COO \\ | \\ C_6H_5.COO \end{matrix} = \begin{matrix} C_6H_5 \\ | \\ C_6H_5 \end{matrix} + \begin{matrix} CO_2 \\ \\ CO_2 \end{matrix}$$

We obtained 80.2 per cent of the theoretical CO_2 and 39.1 per cent diphenyl. Other hydrocarbons were also formed; of these we could identify *p*-diphenyl benzene with certainty.

Similar experiments on decomposition were carried out by E. Lippmann[49]; but this author heated the benzoyl peroxide together with different aromatic hydrocarbons, intending to oxidize the latter. According to the properties of the hydrocarbons, he actually obtained different products.

IX. ALCOHOLS, OLEFINES AND ESTERS ARE FORMED FROM PERACIDS, NOT FROM PEROXIDES.

According to the nature of the acid employed and the conditions of the experiment, Kolbe's electrolytic experiments yield alcohols, olefines or esters, besides the synthetic paraffines. The formation of alcohols discovered by H. Hofer and M. Moest[50] is facilitated in an alkaline electrolyte; but additions of alkali salts of inorganic oxyacids, such as perchlorates, also tend to produce the same effect. The formation of olefines, for instance, strongly predominates in the case of propionates[51], even under those conditions under which acetates give rise to the ethane synthesis with comparative smoothness. Finally, as to the formation of esters, which generally keeps within narrow limits, in the case of trichloro-acetic acid[52], it supersedes all other reactions.

I am dealing with alcohols, olefines and esters conjointly,

[47] H. v. Pechmann and L. Vanino, Ber. d. deutsch. chem. Ges. **27**, 1511 (1894).
[48] Fr. Fichter and A. Fritsch, Helv. chim. acta, **6**, 335 (1923).
[49] Monatshefte f. Chemie, **7**, 525 (1886).
[50] Ann. d. Chemie, **323**, 284 (1902).
[51] J. Peterson, Z. f. physik. Chemie, **33**, 106 (1900).
[52] K. Elbs and J. Kratz, J. f. prakt. Chem., (2) **47**, 104 (1893); **55**, 502 (1897).

because these three classes of substances, as will be seen from the following, are intimately connected.

In attempting to understand the formation of ethylene from propionic acid, by following the hypothesis of the decomposition of discharged anions, we arrive at a peculiar contradiction; whereas, in agreement with Crum Brown and Walker's theory, the normal product butane requires 1 farad to 1 equivalent of propionic acid:

$$\begin{matrix} CH_3 - CH_2 - COO' \\ \\ CH_3 - CH_2 - COO' \end{matrix} + 2 \oplus = \begin{matrix} CH_3 - CH_2 \\ | \\ CH_3 - CH_2 \end{matrix} + \begin{matrix} CO_2 \\ \\ CO_2 \end{matrix}$$

2 farads to 1 equivalent are needed for the formation of ethylene:

$$CH_3 - CH_2 - COO' + 2 \oplus + \tfrac{1}{2}O =$$
$$CO_2 + CH_2 = CH_2 + \tfrac{1}{2}H_2O$$

So, in this case, the discharge of the acid anions would be accompanied by oxidation. However, it is impossible to find a satisfactory explanation for this heterogeneous behavior of acetate and propionate.

We might want to explain the reaction with the aid of H. Hofer and M. Moest's hypothesis[53] concerning the electrochemical formation of alcohols. According to their view, the formation is brought about by the *simultaneous* discharge of acid anions and hydroxyl anions:

$$CH_3.CH_2.COO' + OH' + 2 \oplus = CH_3.CH_2.OH + CO_2$$

It would only have to be assumed that in the case of propionic acid alcohol is replaced by its dehydration product, ethylene.

We might argue that in their electrolysis Hofer and Moest stimulate the formation of alcohol by an addition of perchlorate, that is, a salt, the solution of which contains no hydroxyl ions; that, furthermore, the electrolytic formation of ethylene from propionates takes place in a solution which is acidified with propionic acid, and consequently is deficient in hydroxyl ions[54]; and lastly, that it is highly improbable that the discharge of the

[53] Ann. d. Chemie, 323, 285 (1902).
[54] Zimmermann, Diss. Giessen, 1899.

aliphatic acid anion and of the hydroxyl ion is, at the same anode potential, exactly in the ratio of 1:1. Aside from all this, there is a more lucid, and, I believe, both simple and comprehensive way of explaining the formation of the three classes of substances under the above heading, namely, by interpreting these reactions as oxidations at the carboxyl group.

Besides the acid peroxides, the peracids have also, in recent years, become better known; these also are unstable and highly oxygenous substances. Starting with the acids, the formation of the peracid requires twice as much oxygen as the acid peroxides. Thus the oxidation of aliphatic acid to the peroxide requires 1 farad to 1 equivalent:

$$\begin{matrix} R-COOH \\ \\ R-COOH \end{matrix} + O + 2\,\text{Farad} = \begin{matrix} R-COO \\ \quad | \\ R-COO \end{matrix} + H_2O$$

[Here we have disregarded the complicated dehydration which probably first occurs.] But the oxidation of aliphatic acid to the peracid requires 2 farads to 1 equivalent:

$$R-COOH + O + 2\,\text{Farad} = R-COOOH$$

This clearly explains the difference in the amount of current necessary in the case of acetate and propionate.

The peracid formed, R.COOOH, has, in turn, a strong tendency for further decomposition. By preparing perpropionic acid according to J. d'Ans and W. Frey[55], we managed to perform the explosion in a little steel bomb at about 110°. Depending upon the percentage of peracid which the preparations contained, decomposition took place either more or less violently; in the latter case alcohol was produced besides carbon dioxide, whereas in the former case we obtained ethylene[56], besides carbon dioxide, according to the sequence of the two reactions:

$$CH_3.CH_2.COOOH = CH_3.CH_2.OH + CO_2;$$
$$CH_3.CH_2.OH = CH_2 \Longrightarrow CH_2 + H_2O$$

In offering this interpretation we can again refer to an older

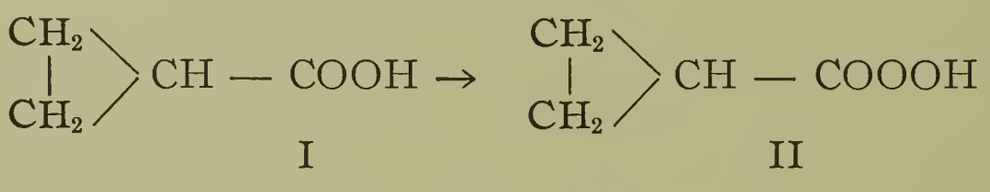
[55] Ber. d. deutsch. chem. Ges., **45**, 1850 (1912).
[56] Fr. Fichter and Eduard Krummenacher, Helv. chim. acta, **1**, 157 (1918).

investigation by A. M. Clover and A. C. Houghton[57] who obtained acrylic acid from the demilateral succinic peracid via β-oxypropionic acid,

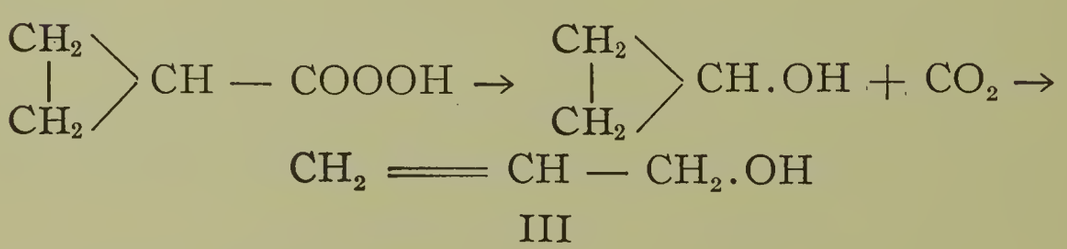
$$HOOC.CH_2.CH_2.COOOH \rightarrow HOOC.CH_2.CH_2.OH + CO_2$$
$$\rightarrow HOOC - CH \equiv CH_2$$

The electrochemical counterpart to this reaction is represented by the formation of ester of acrylic acid in electrolyzing the salts of the acid succinic ester, as recorded by Crum Brown and Walker[58], and the formation of esters of oxyacids as accessory products in the same reaction, as investigated by Bouveault[59] and by Crichton.[60]

In an attempt to subject the alkaline salts of cyclopropane carboxylic acid (I) to Kolbe's synthesis, the product obtained was the allyl ester of cyclopropane carboxylic acid (IV); the cyclopropanol (III) which is first formed is evidently at once rearranged to allyl alcohol.[61] We assume that here also the corresponding peracid (II) is formed first, which is then decomposed by splitting off carbon dioxide. As we carried out the electrolysis with an intentionally ample addition of free cyclopropane carboxylic acid[62], the alcohol was surrounded by enough free acid to be converted immediately into the ester[63] under the dehydrating action of the anode.



I II



III

[57] Am. Chem. J., 32, 43 (1903).
[58] Ann. d. Chemie, 274, 55 (1893).
[59] Bull. Soc. chim. de France, (3) 29, 1043 (1903).
[60] J. of the Chem. Soc., London, 89, 929 (1906).
[61] M. Kishner, J. Soc. phys. chim. russe, 37, 304 (1905).
[62] Hoping thus, but unfortunately in vain, to avoid basic reaction, and to keep within the limits of Kolbe's reaction.
[63] Fr. Fichter and Hans Reeb, Helv. chim. acta, 6, 450 (1923).

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!\rangle CH - COOH + CH_2 = CH - CH_2.OH =$$

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!\rangle CH - COO.CH_2 - CH \!=\!= CH_2 + H_2O$$

IV.

We tested the usefulness of this hypothesis by carrying out experiments with the more easily accessible butyric peracid[64],

$$CH_3.CH_2.CH_2.COOOH.$$

Upon decomposing the latter by gentle heating, after dilution with butyric acid and concentrated sulfuric acid, we obtained, besides a great quantity of carbon dioxide, 69 per cent of the possible amount of propyl ester of butyric acid. Judging from the percentage of peracid, the ester has been formed according to:

$$CH_3.CH_2.CH_2.COOH + CH_3.CH_2.CH_2.COOOH = CO_2 + CH_3.CH_2.CH_2.COO.CH_2.CH_2.CH_3 + H_2O.$$

With the aid of anhydrous hydrogen peroxide it is possible to obtain from the anhydride of trichloro-acetic acid an unstable trichloro-acetic peracid; this, however, is decomposed by the slightest rise in temperature, with an intermediate formation of trichloro-methyl alcohol, which, in turn, is apt to decompose, and only its decomposition products could be isolated, *viz.*, phosgene and hydrochloric acid[65]:

$$CCl_3.COOOH = CCl_3.OH + CO_2$$
$$CCl_3.OH = COCl_2 + HCl$$

In the electrolysis of the trichloro-acetates, following K. Elbs and J. Kratz[66], the ester is obtained instead of the alcohol. The former, however, is also very unstable, and, if decomposed accord-

[64] J. d.'Ans and W. Frey, Ber. d. deutsch. chem. Ges. **45**, 1845, 1850 (1912); J. d'Ans and A. Kneip, Ber d. deutsch. chem. Ges., **48**, 1141 (1915).

[65] Fr. Fichter, A. Fritsch and P. Müller, Helv. chim. acta, **6**, 502 (1923).

[66] *loc. cit.*

ing to our method, yields phosgene and hydrochloric acid, besides trichloro-acetic acid, but no carbon dioxide:

$$CCl_3.COO.CCl_3 + H_2O = CCl_3.COOH + COCl_2 + HCl$$

All these experiments corroborate our assumption that the aliphatic acids are, on the one hand, oxidized to peroxides at the anode, and, on the other other hand, to peracids; that the peracids in decomposing yield, besides carbon dioxide, also alcohols, some of which, according to their structure, are not very stable, splitting off water and changing into olefines; whereas others combine more or less readily with the acid, which is invariably liberated at the anode, to form esters. From the fact that the formation of the peracid requires double the amount of current or double the quantity of oxygen than the formation of peroxides, it must not be concluded that the peracids are generated with greater difficulty that the peroxides; quite the reverse is true, for the peracids are formed under more unfavorable circumstances, for instance, in basic solutions[67] or from acids which are unfit for the formation of peroxides. This accounts for the limited range of Kolbe's synthesis of hydrocarbon.

X. ORGANIC COMPOUNDS WITHOUT CARBOXYL GROUPS ALSO FORM PEROXIDES AT THE ANODE.

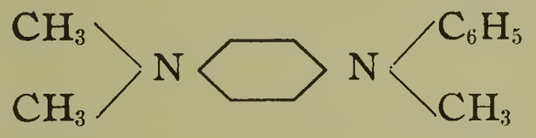
A great many electrochemical oxidations proceed with an intermediate formation of peroxides. The extraordinary oxidizing power of anodic oxygen is especially apt to produce highly oxidized and unstable substances from the most diverse organic starting materials. Dimethyl aniline was first electrochemically oxidized by W. Loeb[68], the result being the formation of tetramethyl benzidine,

$$C_6H_5N(CH_3)_2 \rightarrow (CH_3)_2N \cdot C_6H_4 \cdot C_6H_4 \cdot N(CH_3)_2.$$

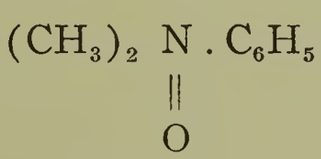
Emil Rothenberger and the writer found[69] that the reaction proceeds much more intricately. The best way is to work with platinum anodes (lead dioxide anodes, which otherwise act less vigorously, in this case cause a greater destruction of the

[67] Perhaps because their formation requires no previous dehydration of the acid.
[68] Z. f. Elektrochem. **7**, 608 (1901).
[69] Helv. chim. acta **5**, 166 (1922).

material and yield more carbon dioxide), employing a current density of 0.02 amp. per sq. cm. in a solution of dimethyl aniline sulfate and an excess of dilute sulfuric acid with external refrigeration. In this way tetramethyl benzidine is obtained with a current yield of 31.9 per cent, after passing 2 farads for every 1 molecule of dimethyl aniline; its formation by nuclear linkage can easily be understood. However, after precipitating the bases tetramethyl benzidine and dimethyl aniline, and the sulfate anions with barium hydroxide, the aqueous filtrate, evaporated to small bulk, is found to contain another base which is easily soluble in water, although insoluble in ether. Upon distillation, this base is converted into the hitherto unknown trimethyl-phenyl-*p*-phenylene diamine:



a substance insoluble in water but easily soluble in ether, with a melting point of 57°. It is a beautifully crystallized weak base, characterized especially by the intense blue color it takes on due to oxidation, even by atmospheric oxygen or by traces of ferric chloride in acid solution. However, this trimethyl-phenyl-*p*-phenylenediamine certainly does not exist in the aqueous solution before distillation. The solution evidently contains a substance of the nature of the aminoxides. It is moreover possible to precipitate from it a small quantity of oxide of dimethyl aniline,

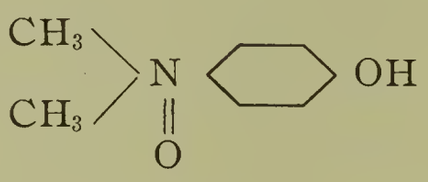


(discovered by E. Bamberger[70]) as a crystalline picrate.

That there is an aminoxide or a similar peroxide in the preliminary stage of the formation of the trimethyl-phenyl-*p*-phenylenediamine is substantiated by the great solubility of the substance in water, its insolubility in ether, its intensely bitter taste, and the explosibility of the compound. Due to the latter, upon distilling *in vacuo* we ruined many a portion; subsequently, however, we left the oxidized solution stand for several weeks before working it.

[70] Ber. d. deutsch. chem. Ges., **32**, 342, 1882 (1899); **34**, 12 (1901); **35**, 1082 (1902); **39**, 4285 (1906).

We have not yet managed to obtain the pure aminoxide in question; thus we can only set up a hypothetical formula, *e. g.*,



If such a substance is to combine with another molecule of dimethyl aniline to trimethyl-phenyl-*p*-phenylenediamine, one of the methyl groups of the latter must give way. This evidently already takes place in part during the electrolysis; for it was possible to detect monomethyl aniline and formaldehyde, the latter as such, as well as in the form of tetramethyl-diamino-diphenyl-methane, which is the condensation product from formaldehyde and dimethylaniline.

In general, it seems safe to assume from the behavior of the dimethyl aniline, the formation of peroxides during electrochemical oxidation of organic substances; as to the aminoxides, these are of the nature of peroxides.

That a peroxide is generated in the electrochemical oxidation of benzaldehyde and can be traced by positive polarization of the anode is shown in another paper by the author[71]. The sphere of peroxides also embraces the quinones which are so frequently obtained as oxidation products.

XI. WHAT DOES BENZENE SULFONIC ACID YIELD AT THE ANODE?

The author and Ernst Stocker[72] subjected benzene sulfonic acid, which is a simple aromatic compound soluble in water, to electrochemical oxidation. We found it best to work with lead dioxide anodes at a current density of about 0.04 amp. per sq. cm., using a clay diaphragm and a double normal solution of benzene sulfonic acid.

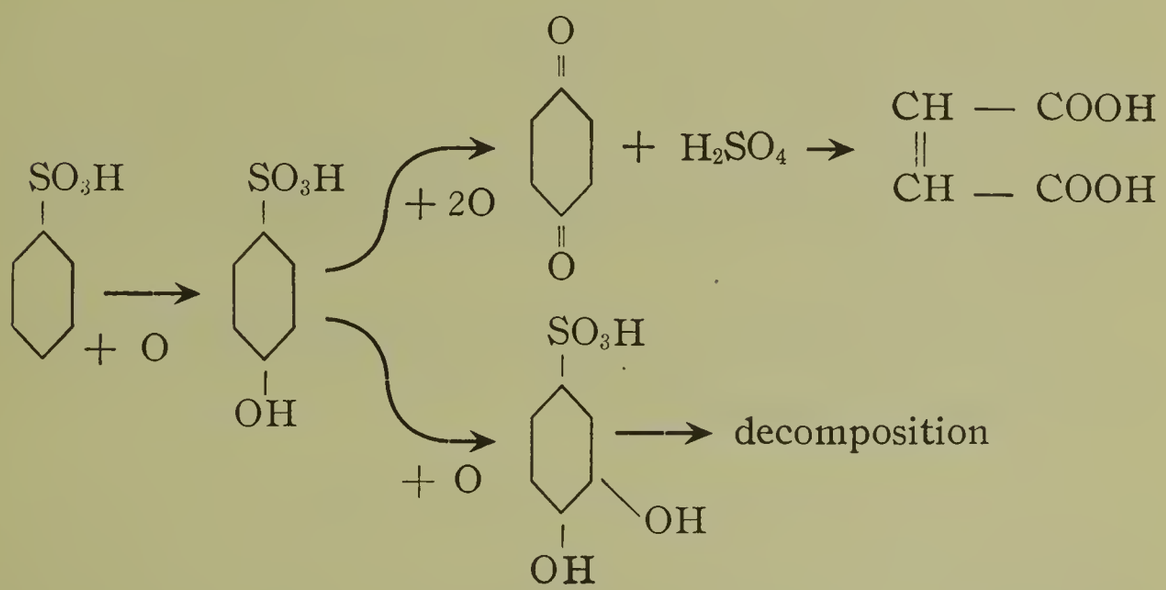
Under these conditions and after passing 4 farads per molecule the following substances can be isolated from the brown-colored electrolyte; by extraction with ether, benzo-quinone and fumaric acid are withdrawn from the solution; with a suspension of barium carbonate, the sulfuric acid formed is then precipitated

[71] Trans. Am. Electrochem. Soc., **45**, 107 (1924).
[72] Unpublished experiments.

from the aqueous solution; basic lead acetate added to the filtrate produces the lead salt of pyrocatechol sulfonic acid. This was detected by the ferric chloride color reaction, the analysis of the barium salt, and the conversion of the latter into barium veratrol sulfonate

$$[C_6H_3(O \cdot CH_3)_2SO_3]_2 Ba$$

The formation of the products hitherto mentioned can easily be understood and brought into an equation[73] which represents an entirely normal process of oxidation:



It must be admitted that this process cannot claim any considerable interest, since the introduction of hydroxyl groups into the aromatic nucleus by means of electrochemical oxidation is well known.

In the above equation the most remarkable factor is missing. At the beginning of the electrolysis, the solution shows oxidizing properties and liberates iodine from a solution of potassium iodide; dissolved ozone or hydrogen peroxide cannot be detected. The oxidizing action might be caused by quinone, but the quinone (aside from the fact that it appears as a decomposition product only in the further course of the electrolysis) can be extracted with ether, which is not the case with the substance in question that liberates iodine.

One might also take into consideration the formation of persulfuric acid, from the sulfuric acid which is liberated in the course of the oxidation. However, this also is not probable, for the quan-

[73] The *p*-phenol sulfonic acid which appears in it cannot yet be traced with certainty.

tities of sulfuric acid are very small, even after continued electrolysis[74], the concentration is low, and consequently, under these circumstances, the formation of persulfuric or Caro's acid is only slight.

We managed at last to prove that the peroxide-like substance generated by the electrolysis loses its oxidizing power much sooner than solutions of quinone or of persulfuric acid. To carry out these experiments under comparable conditions we employed, for the curves registering the decrease of the oxidizing power, some mixtures produced from solutions of benzene sulfonic acid (which, after being electrolyzed, were heated and thus freed from the unstable peroxides), and weighed quantities of quinone or ammonium persulfate; they were compared with newly electrolyzed solutions, and thus the great instability of the unknown peroxide as contrasted with quinone or persulfuric acid became strikingly evident.

These observations led us to consider the possible formation of a peroxide of benzene sulfonic acid. Such a peroxide is known; it is the benzene sulfoperoxide,

$$C_6H_5 — SO_3 — O_3S — C_6H_5$$

prepared from benzene sulfochloride and sodium peroxide by R. F. Weinland and H. Lewkowitz[75]. This substance is soluble in ether, which is at variance with the phenomena observed in the electrolyte. Nevertheless, we investigated the reaction of Weinland's benzene sulfoperoxide, when slowly decomposed in warm water. We obtained phenol and sulfuric acid in the proportion of 1 molecule to 1 molecule; hence the following equation of decomposition:

$$\begin{matrix} C_6H_5 — SO_3 \\ \quad\quad | \\ C_6H_5 — SO_3 \end{matrix} + 2H_2O = \begin{matrix} C_6H_5 \cdot HO \\ \\ C_6H_5 \cdot SO_3H \end{matrix} + H_2SO_4$$

We never found phenol in our electrolytes; but R. Tonoli[76] obtained phenol and sulfuric acid from benzene sulfonic acid,

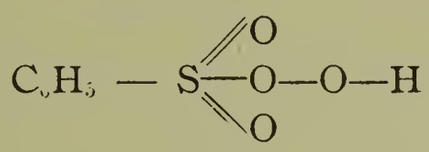
[74] After 36.3 amp. hr. only 5.27 per cent of the theoretical amount of sulfuric acid had been formed from 15.8 grams of benzene sulfonic acid.

[75] Ber. d. deutsch. chem. Ges., 36, 2702 (1903).

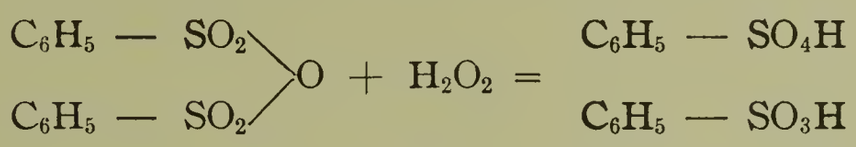
[76] Rendie. Soc. chim. italiana, Fasc. II (1912); Chemiker-Zeitung, 36, 939 (1912).

more than ten years ago, with very high current density (5 amp. per sq. cm.) at platinum anodes. From this it may be concluded that under these conditions benzene sulfoperoxide was produced as intermediate product. Tonoli made his investigations with the hope of finding a benzene sulfoperacid, but was unable to isolate any oxidizing substances in the electrolyte, since the high current density evidently at once caused the peroxide to decompose.

A hitherto unknown peroxide-like substance analogous to Caro's acid can, furthermore, be derived from benzene sulfonic acid:



We tried to get at it by letting benzene sulfonic acid anhydride[77] act upon anhydrous peroxide, according to the reaction:



If the substances mentioned are brought together undiluted, explosion ensues after a few seconds, which shows that a peroxide-like substance of great instability has been formed. Owing to the highly elevated temperature there is a residue of carbonaceous decomposition products; from these, however, it is always possible to extract an acid with water which, like pyrocatechol sulfonic acid, turns intensely green with ferric chloride. Only by adding glacial acetic acid did we manage to slow down the reaction far enough so that the solution simply boiled up and darkened in color. After diluting with water, pyrocatechol sulfonic acid was isolated by precipitation with basic lead acetate, and determined by the analysis of the barium salt.

On the strength of these experiments the following hypothesis, concerning the electrochemical oxidation of benzene sulfonic acid, may be offered: benzene sulfonic acid is oxidized to benzene sulfoperacid at the anode, at current densities such as we selected. The sulfoperacid is very unstable, and insoluble in ether; it lasts

[77] Prepared according to H. Meyer and K. Schlegel, Monatshefte für Chemie, **34**, 561 (1913).

but a short time in a dilute aqueous solution and then rapidly decomposes into pyrocatechol sulfonic acid, according to

$$2C_6H_5 . SO_4H = C_6H_3 (OH)_2 . SO_3H + C_6H_5 . SO_3H$$

The first product of rearrangement to be expected would be *p*-phenol sulfonic acid. The fact that it is not detected may be due to its having been further oxidized by the peracid to pyrocatechol sulfonic acid. It will be possible to elucidate these matters more clearly, if we once succeed in isolating the benzene sulfoperacid.

XII. POSSIBLE USE OF THE HYPOTHESIS OF THE INTERMEDIATE FORMATION OF PEROXIDES.

Hypotheses always have two advantages: they allow of subsuming known facts of a very diverse nature under one common aspect, and they help to predict new and hitherto unknown reactions, thus stimulating further research. In this paper it has been attempted to show that the peroxide hypothesis possesses both advantages, and that it is therefore apt to promote our science.

However, these views may also be of some use in practical electrochemistry. Those engaged in research dealing with electrochemical oxidation of organic compounds find it to be a great disadvantage that the normal and desired reaction is always accompanied by more or less decomposition through oxidation of the organic starting material. This decomposition is undoubtedly due to an intermediate formation of peroxides; if we are able to exclude the peroxides, we shall also stop the decomposition. Therefore, if the investigations here recorded only result in drawing the attention of theoretical and practical workers to the possible existence of an intermediate unstable substance, their object will have been attained; for, if it is once known what causes the deleterious decomposition of the starting material, preventive measures may be introduced.

Basel, October, 1923.

DISCUSSION.

ALEX. LOWY[78]: The peroxide theory I believe has been advanced before. When a mono-basic or di-basic acid is electro-

[78] Prof. of Organic Chemistry, Univ. of Pittsburgh, Pittsburgh, Pa.

lyzed, the anions decompose with the liberation of CO_2. Prof. Fichter emphasizes the formation of an intermediate peroxide, which is substantiated by chemical methods. Prof. Fichter has given us a very good presentation of the possible mechanism of electrochemical oxidation of organic compounds.

A. W. BURWELL[79]: Many organic syntheses are brought about by partial destruction. That is, if you can open a molecule it is subject to combination with another molecule equally open. Kolbe's reaction depends upon that fact, so far as we can see the mechanism of the reaction.

Many an organic reaction, while it may be the principal one occurring in a given case, is not the only reaction that takes place. We do not know how much the side-reactions have to do with the main reaction. There is much in the literature that is stated and taken as fact that may not be fact at all. Interpretations of correctly observed phenomena are often incorrect, so that false conclusions are drawn.

Electrolytically we can get, as Dr. Lowy has suggested, very high concentrations, such as are impossible or at least commercially impossible to obtain by any other means. Is that not, after all, really the answer to the whole problem of organic electrochemistry?

By means of small electrodes or high current densities, we can get almost any concentration we desire of certain elements such as oxygen, hydrogen and others. I think that many reactions can be well explained by this assumption. As an instance, take the oxidation of the paraffines. These bodies do not oxidize readily even on long and intimate contact with air at ordinary concentration (atmospheric pressure). Under pressure, say, of 20 atmospheres, the paraffines are readily and rapidly oxidized. This is more impressive when it is known that pure oxygen under one-fifth of the pressure, or four atmospheres, brings the reaction about with the same speed and facility. On the other hand, the paraffines are not oxidized by chromic acid of a concentration which readily oxidizes toluol and, conversely, toluol is not oxidized by air or oxygen at pressures which rapidly convert the paraffines to fatty acids. These facts, however, I construe as

[79] Consulting Chemist, Jersey City, N. J.

pointing to the possibility that the right concentration has not been used in each of the cases.

C. J. THATCHER[80]: Prof. Nernst pointed out long ago that one could get tremendous pressures, in electrodes, of oxygen or hydrogen. That was one reason why he thought electrolytic processes ought to be capable of further use.

H. C. P. WEBER[81]: I find I cannot go all the way with some of the statements that many of these processes are not "electrochemical." Most of the processes that we call electrochemical processes may also be treated as chemical processes. Thus in the first few words of Prof. Fichter's own paper he says, "Anodic oxygen is probably the most energetic of all oxidizing agents." Now, we may not have a very clear conception of just what anodic oxygen is, but we do know that it is oxygen under a special condition, probably of electrical strain or stress. It is in a specific condition, under which it appears only in electrolytic processes. I think it is proper then to call the results it produces as due to electrochemical oxidation. Now if you are able to prove that there are, perhaps, a few molecules of ozone or a few atoms of monotomic oxygen present under these circumstances, and then proceed to call the process a "chemical reaction," very well; but the conditions under which anodic oxygen appears as such are nevertheless tied up with an electrochemical process, and I think it is still proper to call what happens an electrochemical reaction, even on the basis of Prof. Fichter's own words.

A. W. BURWELL: I think that Dr. Fichter does not hold to the idea that there is no difference whatever between electrolytic and purely chemical reactions. I think the Doctor has the idea that we can produce conditions by the use of the current which are very difficult, and in many cases commercially impossible, to bring about in any other way. For that reason alone it is a valuable study. Dr. Fichter's effort throughout has been to get at the truth and to find the exact mechanism of each reaction.

W. C. MOORE[82]: It seems to me that the points that Dr. Weber and Dr. Burwell brought out open up a very important theme

[80] Chem. Engr. and Electrochemist, New York City.
[81] Research Engr., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.
[82] Res. Chemist, U. S. Industrial Alcohol Co., Baltimore, Md.

to those of us who have had considerable training in electrolytic theory. Oxidation-reduction potentials always are attractive in estimating whether or not a certain solution is going to act as an oxidizing agent. Permanganic acid has an exceedingly high potential, and dichromic acid has a somewhat lower oxidation potential. The point Dr. Weber mentioned may bring up the question as to whether, in a solution of permanganic acid, it is oxygen under very high pressure, giving the high electrical potential, or the permanganate ion.

C. J. THATCHER: That is the point to be determined; it has usually been considered almost impossible to determine, but it is not, I think. I suggested to Prof. Fichter, after I received the manuscript of his paper, a method which I myself used in 1901 to 1903 in Ostwald's laboratory in Leipzig. Prof. Fichter asked me to bring it out in discussion, and it may be of value at this point to explain how it can be used to determine whether an ionic reaction or whether oxygen is involved in such an example. Perhaps I can illustrate it. I was studying, in Ostwald's laboratory, the oxidation of the sulfur acids. Ostwald's idea was that you could start at the lowest stage of oxidation and by controlling the potential go up step by step through thio-sulfuric, tetrathionic, hydro-sulfuric acid and sulfuric acid, simply by controlling the potential. Attacking this problem, I started with sodium thio-sulfate. Ostwald's idea was that S_2O_3 ions would unite to form tetrathionate according to $2S_2O_3'' + 2 \oplus = S_4O_6''$. That is an obvious conclusion to draw. I tried the electrolysis and it did not go that way. At first I got sulfuric acid, but one day, and by chance, I got tetrathionate formed; I think it was about a year before I got it again. However, in the course of that study I hit upon a method to determine what was happening where there is another possible reaction such as this:

$$2S_2O''_3 + \tfrac{1}{2}O_2 + H_2O = S_4O''_6 + 2OH'.$$

Possibly oxygen is involved; that is, that the oxygen, $\frac{1}{2}O_2$, is oxidizing S_2O_3 to S_4O_6. It so happened that during the time of my study Bredig was investigating the effect of poisons on platinum catalysis; and since I was using a platinum anode, I said to myself, if poisons will affect catalytic effects, oxidation

effects, chemically they will do it electrochemically. So I put some poison in my solution. Ostwald did not like the idea of having poison in the electrolyte. Nevertheless when I added mercuric cyanide, I found that I did not get S_4O_6 under conditions which I did otherwise. After a great deal of work I was able to demonstrate that the action which actually does take place, instead of being simply a coupling of S_2O_3 ions, is one in which oxygen was really involved. A great many electrode measurements showed that when you inhibit the action of oxygen by putting in a sufficient amount of poison you could not get this reaction. Consequently, I established that in this case of two possible current reactions, that is simply a coupling of the two ions, electrolytically, or a pure oxidation, that pure oxidation was the one. That idea can be useful, and I think Prof. Fichter is going to use it in his study of this question. I bring it to your attention because it may be a method whereby one or two or more possible reactions can be isolated. You can inhibit pure oxidation phenomena on your electrode if you add sufficient of a negative catalyzer to your electrolyte. I used a concentration of only 0.0001 mol.

F. C. Frary[83]: If we are to consider that the electrolytic reactions at the electrodes are due to the concentration of certain electrolytic products there, I think there is another factor that ought to be emphasized which is often of deciding importance. That is, you not only get the high concentrations at the electrodes but you get these concentrations highly localized, and the phenomena may be analogous to the well-known fixation of nitrogen in the arc; by localizing your concentrations, and by practically immediately removing your reacting substance from that concentration, you may get reactions which you would not get if that concentration were more widely distributed.

C. J. Thatcher: It seems to me that if we hold that point in view we can understand what is going to take place much better. We do not always know what the concentration of the compound or what the substance is, but our aim should be to get the concentration of that particularly effective compound or ion which does the work. If we look at the electrode process

[83] Director of Research, Aluminum Co. of America, New Kensington, Pa.

in that manner it often enables us to bring about the reaction which we desire.

C. J. BROCKMAN[84]: Dr. Ehrich Müller at Dresden has postulated a "dehydroxidation," I believe he calls it, of ethyl alcohol, etc., getting as intermediates oxy-aldehyde and oxy-acid, with a final evolution of hydrogen ions. It looks as if the second equation above (Dr. Thatcher's discussion) is the analog of this. It is unfortunate that we do not have a paper today from Dr. Müller. There seem to be two camps in Europe: the "dehydroxidation" one and the "per-compound" one of Fichter. Fichter claims that the theory of Müller is in accord with his own, but Müller does not admit this.

[84] Univ. of Georgia, Athens, Ga.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 24, 1924, Dr. C. J. Thatcher in the Chair.

THE ELECTROLYTIC PRODUCTION OF COBALT AND NICKEL TRIACETATES FROM THE DIACETATES; THE ELECTROLYTIC OXIDATION OF COBALT AND NICKEL DICHLORIDES.[1]

By C. Schall and H. Markgraf.[2]

Abstract.

Pure cobalt and nickel diacetates were dissolved in absolute acetic acid. The solution was electrolyzed between platinum electrodes, and pure well-crystallized nickel and cobalt triacetates were obtained. These electrolytic oxidation results support the freezing point-lowering determinations and direct chemical analysis, and indicate that the two triacetates have the simple formula $Ni(CH_3COO)_3$ and $Co(CH_3COO)_3$, respectively. Failure in obtaining these triacetates in the past has been found to be due to the presence of small amounts of water in the acetic acid solutions. Nickel and cobalt trichloride were obtained by electrolyzing the dichloride, dissolved in concentrated hydrochloric acid, in a two-compartment cell. Evidence for the probable existence of higher chlorides, such as $CoCl_4$, is presented.

The production of pure crystalline cobalt and nickel triacetates has heretofore not met with success. We believed that failure in the past might have been due to the presence of water and accordingly we carried out tests with anhydrous materials. We prepared anhydrous acetic acid by distilling 99.6 per cent acetic acid (melting point 16.64°) to which had been added a little triacetyl boride[3], in place of B_2O_3.[4]

[1] Manuscript received April 18, 1923. Translated by Colin G. Fink.

[2] Physical Chemical Laboratory, Leipzig University.

[3] A. Pictet and A. Geleznoff, Ber., 36, 2219 (1903). The triacetyl boride is readily prepared. In contradistinction to B_2O_3 it is soluble in glacial acetic acid; it melts at 121°.

[4] Compare methods for the preparation of absolute formic acid. M. C. Boswell and H. E. Corman, Canadian Chemistry and Metallurgy, March, 1922; Chem. Trade J. 70, 359.

The elimination of water is very likely according to the following reaction:

$$B(COO\,CH_3)_3 + 2H_2O = HBO_2 + 3CH_3COOH$$

Metaboric acid has a high boiling point. The distillate showed no trace of boron. A sample of 2.5 g. of the distillate was carefully transferred to a weighing bottle, then diluted to 500 cc. with CO_2-free water and samples of 25 cc. titrated with 0.1N $Ba(OH)_2$ solution. An average of 20.813 cc. of this solution was required, and accordingly the distillate could be regarded as 100 per cent anhydrous acetic acid. The melting point of the product was found to be 17.4°. The specific conductivity was

$$\mu = 0.6 \times 10^{-8} \text{ at } 18°$$

and

$$\mu = 1.1 \times 10^{-8} \text{ at } 25°$$

whereas the values for the original 99.6 per cent acid were approximately 7.0×10^{-8} and 10×10^{-8}, respectively. Kohlrausch and Holborn cite $\mu = 4 \times 10^{-8}$ for a 99.7 per cent acid.[5]

In the following Tables I and II, Λ is the equivalent conductivity, c the temperature coefficient, $\mu_{18°}$ and $\mu_{25°}$ the specific conductivities at 18° and 25° (deducting the conductivity of the solvent), and 1000η the concentration in equivalents per liter. The determinations were made as in the case of the pure lead diacetate.[6] The values for the lead diacetate are included in Table I for the sake of comparison.

We observe that the conductivity of the nickel acetate exceeds that of the others. The lowest conductivity values are those for lead acetate. This salt has also a very low temperature coefficient. The Λ values all show a distinct minimum at $1{,}000\ \eta = 1/8$. The temperature coefficient for this concentration is a maximum in the case of the cobalt and nickel salts. A maximum of the Λ values is noticeable at about $1{,}000\eta = 1/16$. Hopfgartner[7] found similar maxima for the alkali acetates.

[5] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte", 1898, p. 155.

[6] Schall and Melzer, Z. Elektrochem., 28, 474 (1922). The surfaces of the electrodes were 1 sq. cm. and 10.8 sq. cm. respectively.

[7] Monatshefte f. Chemie, 34, 1313 (1913).

TABLE I.

Diacetates of Co, Ni, Pb in 99.6 per cent Acetic Acid.

1000 η	μ 18° × 10^7			μ 25° × 10^7			Λ 18°			Λ 25°		c		
	Co	Ni	Pb	Co	Ni	Pb	Co	Ni	Pb	Co	Ni	Co	Ni	Pb
1	1046.4	1075.2	518.4	1502.2	1587.4	561.7	0.10464	0.10752	0.05184	0.15022	0.15874	0.06222	0.06806	0.01193
½	362.8	443.2	210.6	552.1	666.8	227.6	0.07256	0.08864	0.04212	0.11042	0.13336	0.07453	0.07208	0.01152
¼	76.4	116.0	63.4	114.4	176.3	67.9	0.03056	0.04640	0.02536	0.04576	0.07052	0.0711	0.07420	0.01104
⅛	32.6	37.6	30.7	50.3	57.5	32.4	0.02608	0.03008	0.02456	0.04024	0.04600	0.0776	0.0757	0.00791
1/16	21.6	24.2	16.9	31.6	34.7	17.4	0.03456	0.03872	0.02704	0.05056	0.05552	0.0661	0.0701	0.00423
1/32	8.8	9.2	6.5	12.5	13.4	6.8	0.02816	0.02944	0.02070	0.04000	0.04288	0.060	0.066	0.0068

TABLE II.

The Same Diacetates in Absolute Acetic Acid.

1000 η	μ 18° × 10^7			μ 25° × 10^7			Λ 18°			Λ 25°		c		
	Co	Ni	Pb	Co	Ni	Pb	Co	Ni	Pb	Co	Ni	Co	Ni	Pb
½	...	...	52.3	...	...	56.8	.....	.....	0.01046	.....	.....	.....	.....	0.0123
¼	...	...	15.7	...	...	16.8	.....	.....	0.00628	.....	.....	.....	.....	0.0100
⅛	8.4	9.4	7.5	10.9	12.3	7.7	0.00672	0.00750	0.00600	0.00872	0.00984	0.043	0.044	0.0038
1/16	4.4	6.1	4.2	5.7	7.8	4.3	0.00704	0.00971	0.00672	0.00912	0.01248	0.042	0.043	0.0029
1/32	2.1	2.3	1.3	2.7	3.0	1.6	0.00672	0.00736	0.00416	0.00864	0.00960	0.041	0.042	0.0033

We next prepared anhydrous cobalt and nickel diacetates according to Spaeth's method.[8] Concentrated solutions of the cobalt and nickel were prepared in the 100 per cent anhydrous acetic acid heated to 65°. The normality of the cobalt solution was found to be 0.1932 and that of the nickel solution, 0.1971.

Samples of 25 cc. of these solutions were electrolyzed for 6 hr. between platinum electrodes at 96 to 99 v., 0.007 to 0.009 amp. The temperature of the electrolyte was maintained at 65°. The apparatus used is illustrated in Fig. 1. All access of moisture was avoided. The escape of acetic acid vapors was prevented by attaching to the apparatus two water-cooled condensers not shown in the figure. The electrolyzed solutions were carefully evaporated in a P_2O_5 dry vacuum. Well defined green crystals remained behind which, upon analysis, proved to be pure Co- and Ni-triacetates. The following electrolysis of the cobalt and nickel diacetates was carried out without diaphragms to avoid interference due to electro-endosmosis and increase in electrical resistance.

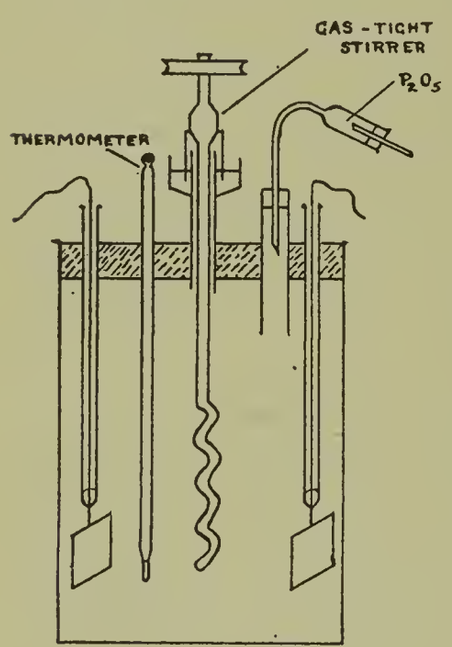


FIG. 1

In Tables III and IV the results obtained upon electrolyzing the cobalt and nickel diacetate solutions are summarized. The current was kept nearly constant throughout, and was checked every hour by weighing the silver cathode of the coulometer (column 5, Tables III and IV). The increase in weight at the end of every hour, due to deposition of cobalt (or nickel) on the platinum cathode of the cell is recorded in the sixth column[9]; the seventh column shows the ratio of atoms of silver to atoms of cobalt (or nickel).

This seventh column indicates that the valence of the cobalt (or nickel) was 2 during the first 2 hours, and then during the

[8] Monatshefte f. Chemie, 33, 235 (1912).

[9] There is only a very slight tendency for the deposited cobalt or nickel to go back into solution. Allowing the cells to stand idle without current passing through, only 0.0021 gram of Co (or Ni) were dissolved in 4 hours. The cobalt and Ni acetate solutions are much more stable than the corresponding iron salts. Nevertheless great care was exercised in weighing the cobalt and nickel deposits to avoid all error due to surface oxidation.

TABLE III. *Results of Electrolyzing Cobalt Diacetate.*

Two g. material = 0.0113 Mols Diacetate = 0.6662 g. Co dissolved in 50 cc. 99.6% CH_3COOH. Pt Anode 6.5 sq. cm.; cathode, 1 sq. cm. exposed surface

t Min.	Temp. Degrees	Volts	Amp. x 10^3	Silver increase in grams.	Cobalt increase in grams	Atoms Ag / Atoms Co	cc. *N*/100 Thiosulfate: For 1 cc. of solution after t min.	cc. *N*/100 Thiosulfate: Calculated for total orig. vol.	Atoms I / Atoms Co	Mols. Triacetate in orig. vol. after t min.
0	16	98	47	.....	.....	....	...	...	....	.....
60	17	98	47	0.1912	0.0523	1.999	3.54	177	1.999	177×10^{-5}
120	17	96	48	0.1911	0.0521	2.000	7.15	176	2.000	353×10^{-5}
180	18	99	47	0.1913	0.0465	2.249	9.20	98	1.249	451×10^{-5}
240	18	98	47	0.1911	0.0418	2.499	9.95	35	0.500	486×10^{-5}
300	19	97	48	0.1914	0.0380	2.798	9.60	—16	—0.249	470×10^{-5}
360	17	99	48	0.1913	0.0348	3.000	8.28	—59	—1.003	411×10^{-5}
420	18	97	49	0.1910	0.0348	2.998	6.94	—59	—1.000	352×10^{-5}
480	19	98	47	0.1911	0.0348	3.000	5.54	—59	—1.000	293×10^{-5}

TABLE IV. *Results of Electrolyzing Nickel Diacetate.*

Conditions same as in Table III.

t Min.	Temp. Degrees	Volts	Amp. x 10^3	Silver grams	Nickel grams	Atoms Ag / Atoms Ni	cc. *N*/100 Thiosulfate: For 1 cc. of solution after t min.	cc. *N*/100 Thiosulfate: Calculated for total orig. vol.	Atoms I / Atoms Ni	Mols. Triacetate in orig. vol. after t min.
0	18	99	49	.....	.....	....	...	...	....	.....
60	19	98	49	0.1965	0.0534	2.001	3.64	182	2.010	182×10^{-5}
120	17	94	49	0.1965	0.0526	2.000	7.35	182	2.041	364×10^{-5}
180	18	99	48	0.1979	0.0478	2.248	9.48	102	1.258	466×10^{-5}
240	19	96	47	0.1953	0.0427	2.502	10.25	36	0.502	502×10^{-5}
300	19	95	49	0.1963	0.0382	2.799	9.90	—16	—0.251	486×10^{-5}
360	19	98	49	0.1993	0.0361	3.003	8.52	—62	—1.004	424×10^{-5}
420	18	99	49	0.1938	0.0351	3.000	7.16	—60	—1.006	364×10^{-5}
480	18	99	48	0.1969	0.0356	3.001	6.72	—62	—1.010	302×10^{-5}

next 3 to 4 hours changed over to the trivalent cobalt (or nickel). What probably happens is this:

At the beginning of the electrolysis, a divalent ion, Me_1^{++}, gives up two positive charges at the cathode and at the same time two Me^{++} ions take on two charges: $2Me^{++} = 2Me^{+++}$ at the anode. Out of three divalent metal ions, Me^{++}, one is precipitated and two are raised to trivalent ions Me^{+++}. As the concentration of triacetate increases, the reaction $Me^{+++} + 3 \ominus = Me$ will take place at the cathode and the reaction $3Me^{++} + 3 \oplus = 3Me^{+++}$ at the anode. Assuming 100 per cent current efficiency, it follows that $\frac{2}{3}$ of all of the diacetate mols are transformed into triacetate mols. We may represent the quantity of triacetate mols formed by the ratio $2g/A_{me}$ where g is the weight in grams of metal (Co or Ni) deposited and A is the atomic weight in grams of the metal. Besides the reaction $Me^{++} \rightarrow Me^{+++}$ at the anode, some acetate ions are discharged and as soon as the divalent metal ions have disappeared entirely the acetate ion discharge will be the only reaction at the anode; that is, we shall then have merely triacetate electrolysis.

During the electrolytic oxidation of diacetate to triacetate, the cobalt solution changes color, from red to green, and the nickel solution from light green to dark green.[10]

Column 8 of Table III records the cubic centimeters of $N/100$ thiosulfate solution required to react with the iodine liberated in 1 cc. of the electrolyte (saturated with sodium acetate) by the introduction of a KI solution; and column 9 the corresponding calculated number of cc. of $N/100$ thiosulfate for the original volume of electrolyte[11]. Column 10 represents the ratio of atoms of iodine to atoms of cobalt (or nickel). At $t = 240$ min. the largest number of triacetate mols formed, 486×10^{-5} (last column) corresponds to $0.0523 + 0.0521 + 0.0465 + 0.0418 = 0.1927$ grams deposited on the cathode, or $\frac{2(0.1927)}{58.97} = 0.00652$ mols of triacetate. In other words, $0.00486/0.00652 = 74.3$ per cent of the total number of triacetate

[10] B. R. Stanley, J. Am. Chem. Soc. 28, 177 (1906), observed the change of green to red in the reduction of cobalt oxalate solutions.

[11] Z. f. Elektrochem., 22, 422 (1916).

mols were produced at t = 240 min. The maximum triacetate output would therefore correspond to 0.2221 grams of cobalt, or 0.00753 cobalt triacetate mols. The results for nickel are practically the same as for cobalt except that the maximum 502×10^{-5} mols acetate is somewhat higher than that for cobalt. The evolution of gas at the anode becomes noticeable at t = 240 with either metal acetate.

As the time increases the thiosulfate values (column 9) pass through zero, indicating that at this point the amount of triacetate formed is equal to the amount decomposed; thence these values become negative and likewise the corresponding values of column 10. The three last constant values of column 9 correspond to the constant values of column 6, that is, the electrolysis is confined to that of *tri*-acetate.

We found no indications, either during electrolysis or later upon evaporation and crystallization of solutions, that a tetra-acetate of cobalt or nickel is formed or exists. Five grams of cobalt triacetate carefully recrystallized produced small apple green crystals that looked like octahedrons. The corresponding nickel acetate crystals were brownish-green. Both crystals decomposed and blackened upon heating to 100° C. Upon introducing them into CO_2-free water (30 to 50 parts water to 1 of triacetate) the salts hydrolyzed readily, forming oxyhydrates and acetic acid, as was verified analytically. Assuming the molecular weight to be 236.07 for cobalt triacetate, on the basis of the simple formula $Co(CH_3COO)_3$, and 235.78 for the nickel triacetate, $Ni(CH_3COO)_3$, and dissolving each salt in anhydrous acetic acid we obtained the value K = 39 for the constant in the freezing point lowering determinations, a value that corresponds closely to that obtained by H. C. Jones in his measurements of sodium acetate in acetic acid of a melting point 16.5.[12] Accordingly, the electrolytic values, direct chemical analyses of the two salts and freezing point lowering determinations, all point to the simple formula $Co(CH_3COO)_3$ and not to formulæ such as $[Co_3(CH_3COO)_6]$ $(CH_3COO)_3$ advanced by others.[13]

In Table V we have summarized results of our experiments

[12] H. C. Jones, Z. Physikal. Chem. 13, 435 (1894).
[13] S. R. F. Weinland and H. Reihlen, Z. anorg. Chem. 82, 426 (1913).

to show that the electrolytic production of the two triacetates is only possible if the solvent is sufficiently anhydrous. Starting with our standard anhydrous acetic acid, we added in turn 5, 10 and 15 parts of water per 1,000 cc. of acid. Readings were taken every half hour. As is evident, the introduction of water

TABLE V.

Summary of Results.

Eighty g./L. of 99.6 per cent acetic acid. Other conditions same as those in Table III.

Co Diacetate

t. in minutes.	0	30	60	90	120	150	180	210	240
Temp. C.....	16°	18°	21°	22°	26°	24°	24°	26°	28°
Water added, per cent ...	. .	none	0.5	none	none	1.0	none	1.5	none
Volts	96	98	97	78	79	89	92	89	88
Amp. x 10^3 ..	76	82	80	181	192	210	421	392	416
cc. $N/100$ thios.	.	286	295	312	305	651	—98	970	69
Mols. triacetate x 10^5 ..	. . .	286	581	893	1,198	1,849	1,751	2,721	2,790

Ni Diacetate

Temp. C.....	17°	18°	19°	20°	21°	19°	21°	20°	18°
Volts	96	98	94	92	99	86	75	77	91
Amp. x 10^3 ..	79	79	80	180	195	218	421	433	431
cc. $N/100$ thios.	. . .	281	278	330	304	656	—103	967	—16
Mols. triacetate x 10^5 ..	. .	281	559	889	1,193	1,849	1,746	2,713	2,697

NOTE:—In the above table the values for both the "cc. $N/100$ thiosulfate" and the "mols. of triacetate x 10^5" are on the basis of the original volume of electrolyte.

caused a rise in current, but in spite of this increase in farads the thiosulfate values remain practically constant during the first two hours; however, during the interval, 120 min. to 150 min., the thiosulfate value has more than doubled, and during 180 min. to 210 min. the value has increased to more than three-fold. Here we are no longer dealing with pure triacetate formation. Upon evaporating the electrolyte, at the end of 240 minutes of electrolysis, we obtained no well-defined crystals but merely a green

syrupy mass. Even when the acetic acid contains as little as 1 per cent H_2O, these amorphous green masses are obtained.[14]

Mr. Anders of my laboratory repeated the borontriacetate method of preparing anhydrous acetic acid (see page 161), starting out with other lots of acid. However, the melting point of his products was appreciably lower, ranging between 16.5° and 16.6° C., instead of 17.4°, and the specific conductivities were 3.2×10^{-8} at 18° and 4.7×10^{-8} at 25°. This acid was used in the following experiments.

In these, it was found that a mere trace of moisture increases the velocity of the formation of the triacetate, and it seems safe to conclude that even the 17.4° melting point acid still contained enough H_2O to bring about a fairly rapid formation of nickel and cobalt triacetates. As the reaction proceeds, and as the trace of H_2O probably disappears, the velocity drops down considerably —an observation also made in the case of the formation of lead tetra-acetate from the diacetate.[15] Furthermore, a slight evolution of gas at the anode was discernible as the reaction proceeded, possibly due to discharge of acetate ions.

Referring to Table III, page 165, the results seem to be dependent upon the physical structure and the degree of passivity[16] of cathodically precipitated cobalt. The first stages of the experiments were readily reproducible, using the 16.5° melting point acid, but in the subsequent stages more or less of the cathodic cobalt went into solution.

Some advantage was gained by inclosing the cathode and cooling coil in a porous cell, and counteracting the electro-endosmosis by increasing the pressure on the solution inside the cell.[17]

As regards the passivity of nickel in acetate solution,[18] it was possible, with the 16.5° melting point acid, to reproduce the earlier stages of the experiments with the 17.4° melting point acid (Table IV). However, we could not get a current efficiency better than 20 per cent of the theoretical nickel triacetate yield, even with a diaphragm. Furthermore, an inferior output of

[14] Cf. Bauer, Dissertation, Giessen 1897; H. Copaux, Ann. chim. phys. (8) 6, 508 (1905). Furthermore, in the presence of traces of water a distinct blackening of the anolyte has been observed by us.

[15] C. Schall and W. Melzer, Z. f. Elektrochem., 28, 495 (1922).

[16] S. R. Mueller, Elektrochemie nichtwässr. Lösungen, p. 114 (1923).

[17] C. Schall, Z. f. Elektrochem., 21, 70 (1915).

[18] M. Le Blanc u. M. G. Levi, Boltzmann Festschrift, 183 (1904).

nickel triacetate crystals was obtained as compared with the product from the runs using the 17.4° melting point acetic acid. We intend to try experiments keeping the anolyte at 8° and using the 16.5° acid.

THE ELECTROLYTIC OXIDATION OF COBALT AND NICKEL DICHLORIDES.

Dark green solutions of the pure trioxides of cobalt and nickel (derived from the hydrolytic decomposition of the pure triacetates) were prepared in two ways: (1) Co_2O_3 was introduced into absolute ethyl alcohol through which HCl gas was bubbled; and (2) Ni_2O_3 was introduced into a concentrated aqueous solution of HCl (sp. gr. 1.19), keeping the solution at as low a temperature as possible, to avoid the thermal decomposition of the chloride,[19] such as:

$$2CoCl_3 \leftrightarrows 2CoCl_2 + Cl_2$$

The above solutions were carefully evaporated down to small bulk at —15 to —20° C. and transferred at once (without exposing them to moist air) onto glass plates and these placed into a desiccator charged with $CaCl_2$, P_2O_5 and NaOH. The desiccator was kept imbedded in a salt-ice freezing mixture.

Starting out with Co_2O_3, we obtained from the alcohol-hydrochloric acid solutions distinct green crystals of what we believe to be $CoCl_3$. It does not seem probable that these crystals corresponded to any complex salt of cobalt trichloride and HCl, as such complexes are known not to form in the case of the dichloride.[20]

Starting out with Ni_2O_3 dissolved in concentrated HCl,[21] we likewise obtained distinct green crystals. As in the case of the cobalt salt crystals, the nickel crystals readily reacted with starch-iodide, liberating iodine. The nickel salt was undoubtedly $NiCl_3$.

We next treated the dichlorides of cobalt and nickel with liquid chlorine, but could not detect any reaction taking place. However, chlorine gas introduced into the blue alcoholic solution of the anhydrous cobalt dichloride (0.1 g. $CoCl_2$ in 4 cc. absolute ethyl alcohol plus 1 drop of water), which was cooled[22] to

[19] Just as in the case of $MnCl_3$. See M. Sem. Z. Elektrochem., **21**, 431 (1915).
[20] S. H. W. Foote, J. Am. Chem. Soc., **45**, 665 (1923).
[21] The alcohol-hydrochloric acid solution of Ni_2O_3 is not stable.
[22] CO_2 + ethyl alcohol.

—60° C. in order to reduce to a minimum the interaction between chlorine and alcohol, transformed the solution into an almost opaque green solution. Upon cooling the solution down to —75° and introducing additional quantities of chlorine, a clear transparent orange solution was obtained. As the temperature of the solution was raised—by merely taking the reaction vessel out of the Dewar flask—its color changed instantly back to green and then to blue. Upon cooling, the solution again turned blue and then orange. The same color changes were observed in the case of the solution of $CoCl_2$ in concentrated HCl, (4–5 cc. of 1.19 sp. gr. HCl to 0.2 g. of $CoCl_2$) except that a brown crystalline precipitate separated out of the orange solution. This precipitate turned green with rise in temperature, passing back into solution. Upon further increase in temperature, the green solution turned blue. It is barely possible that a chloride exists of a higher stage of oxidation, say a tetrachloride, $CoCl_4$, corresponding to CoO_2. It ought to be possible to establish this point by determining the Co : Cl ratio. Furthermore, it seems probable that this higher chloride, say $CoCl_4$, can be produced electrolytically, since even dilute solutions of $CoCl_2$ in concentrated HCl, when cooled down to —60° C. and electrolyzed, turn orange at the anode.

Similarly, when we electrolyzed a cold solution of $NiCl_2$ (0.3 g. in 3 to 4 cc. of HCl, sp. gr. 1.19), the anolyte first turns a deep blue-green, no matter whether or not chlorine gas is present in the solution. Upon further electrolysis at —70° C. and in the presence of an excess of Cl gas in solution, the anolyte takes on a light bluish-green color. After continuing the electrolysis for some time and passing Cl gas through the solution, a layer of liquid chlorine collected below the nickel solution. In thin layers, this liquid has a reddish hue; in thicker layers it was whiter than pure liquid chlorine, due probably to the presence of dissolved $NiCl_3$, which is probably stable under these conditions. The catholyte was contained in a porous clay cell. The electrodes were platinum with 11 sq. cm. of exposed anode and 1 sq. cm. of exposed cathode.

All nickel salts used in our experiments were "cobalt-free"; likewise all cobalt salts were "nickel-free."

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DISCUSSION.

ALEX. LOWY[22]: In oxidizing nickelous to the nickelic chloride electrolytically, Schall had used platinum anodes in concentrated hydrochloric acid. This is a chlorination reaction. Do you think there is any possibility of getting some platinum chloride into that mixture? If so, it would act as a halogen carrier.

COLIN G. FINK[23]: Undoubtedly some platinum chloride. If you electrolyze a chloride with a platinum anode, you always will. Your question leads up to a second, namely, what is the catalytic effect of platinum chloride. There are a number of reactions which are not brought about readily without the presence of platinum chloride.

W. C. MOORE[24]: Dr. Lowy's question reminds me of a point that comes up here. A number of years ago I had occasion to dispose of chlorine set free electrolytically in small quantities. It was purely a laboratory experiment, and I solved that problem by coating the platinum gauze electrode with spongy silver. The silver chloride formed prevented the electrode being attacked. You can readily clean the electrode after the reaction is over, by dissolving the silver chloride in ammonia water.

H. C. P. WEBER[25]: In the case of hard or massive platinum foil, chlorine will dissolve platinum very slowly. Of course, theoretically, there will be some platinum chloride formed, but the quantity may not be appreciable.

C. J. THATCHER[26]: It takes very little of a metallic compound of that sort to act catalytically. I remember that Titoff a great many years ago found that a concentration of copper, I think of 1 mol. in a million liters, would double the rate of oxidation of sulfites to sulfates by air. It was in inconceivably small concentration. He had great difficulty in getting copper-free water in order to study the reaction.

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[23] Head, Division of Electrochemistry, Columbia Univ., New York City.
[24] Research Chemist, U. S. Industrial Alcohol Co., Baltimore, Md.
[25] Research Engr., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.
[26] Chem. Engr. and Electrochemist, New York City.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 24, 1924, Dr. C. J. Thatcher in the Chair.

ELECTROLYTIC REDUCTION OF ACID-OXIMES.[1]

By Masayoshi Ishibashi.[2]

Acid-oximes are more or less easily hydrolyzed in an acid solution, and some of them, such as γ-isonitroso-valeric acid, are so readily hydrolyzable that they cannot be chemically reduced to the corresponding amines.

In the electrolytic process, however, as it is possible to control the temperature and the concentration of acid without much difficulty, smoother reduction may be expected.

With this expectation the electrolytic reduction of γ-isonitroso-valeric acid and α-isonitroso-propionic acid in a sulfuric acid solution was studied, and the most favorable conditions for reduction and best yield of amines were determined as follows:

Current density	γ-isonitroso-valeric acid 2 amp./sq. dm.	α-isonitroso-propionic acid 4.5 amp./sq. dm.
Temperature C.....	3-5°	7-10°
Concentration of H_2SO_4.....	5 per cent	8 per cent
Yield (material)	84 per cent	95 per cent
Yield (current).....	61 per cent	93 per cent

From the above table it is clearly seen that γ-nitroso acid is more apt to undergo hydrolysis even in a more dilute sulfuric acid solution, with a smaller current density and at a lower temperature, as compared with α-nitroso acid.

The details of the work will shortly be published in the Memoirs of the College of Science, Kyoto Imperial University.

DISCUSSION.

Alex. Lowy[3]: Because the author gives the percentage yield of the product and the current yield, it does not necessarily follow

[1] Manuscript received March 27, 1924.
[2] College of Science, Kyoto Imperial University, Kyoto, Japan.
[3] Prof. of Organic Chemistry, Univ. of Pittsburgh, Pittsburgh, Pa.

that, "from the above table it is clearly seen that the γ-nitroso acid is more apt to undergo hydrolysis," because there are several other side reactions possible. Other reactions may be going on at the same time which would decrease that yield.

COLIN G. FINK[4]: Those of you who are particularly interested in the organic electrochemical field will find it worth while to look up the "Memoirs of the College of Science." A large percentage of the papers published in these memoirs are organic electrochemical.

ALEX. LOWY: Also the Japanese National Research Council has a publication, which contains a number of papers pertaining to organic electrochemistry.

[4] Head, Division of Electrochemistry, Columbia Univ., New York City.

This paper comprises the subject matter of an address delivered before the New York section of the American Electrochemical Society, November 16, 1923, Mr. P. D. V. Manning in the Chair.

THE PROPERTIES OF THE ELEMENTS IN THE ELECTRONEGATIVE CONDITION.[1]

By Charles A. Kraus.[2]

Abstract.

The properties of compounds are largely determined by the electro-affinity of their constituent elements. The elements may be arranged in a twofold series of electro-affinity, positive and negative respectively. Elements of intermediate electro-affinity occur in both series. Such elements may be termed amphoteric. Ordinarily most of these amphoteric elements are known only in the electropositive condition. They may, however, be obtained in the electronegative condition in suitable solvents, such as, for example, liquid ammonia. The compounds of many of these elements with strongly electropositive elements, such as the alkali metals, are soluble in liquid ammonia. These solutions are electrolytic in their properties. The less electropositive elements act as anions and may be precipitated on the anode in coherent form. In the pure state these compounds are metallic in their properties. The simple anions of the amphoteric elements form complex anions by interaction with the pure elements. For example, lead forms an anion in which nine atoms of lead are associated with four negative charges. From a solution of this compound 2.25 atoms of lead are precipitated on the anode per equivalent of electricity. Compounds of other amphoteric elements exhibit corresponding properties. Solutions of anions of amphoteric elements enter into various reactions characteristic of electrolytes. Anions of this type are also formed by the action of weak electrolytes on the pure metals. Thus potassium amide reacts with tin to form a potassium stannide and potassium ammono-stannite. The reaction is analogous to that of potassium hydroxide with

[1] Revised manuscript received March 3, 1924.

[2] Director of Laboratories, Clark University, Worcester, Mass.

chlorine, in which potassium chloride and potassium hypochlorite are initially formed. Some data are given as to the free energy of formation of metallic compounds.

The elements differ from one another in their affinity for the electrical charge, that is, for the negative electron; and the properties of the elements, as well as many of the properties of their compounds, admit of interpretation in terms of their electro-affinity.

While the precise position of all the elements in the series of electro-affinities is not known, the approximate order of the greater number of elements may be determined by various means. Perhaps the most satisfactory method is to arrange the elements in the order of the energy effects accompanying the formation of their compounds with a given element. Thus, we may arrange them in the order of the heat of formation of their chlorides, which, inasmuch as most of these compounds are solids and liquids at ordinary temperatures, gives us an approximate measure of their free energy of formation. If we determine the order of the elements in this way, we find that it agrees fairly well with that of the electrode potentials, except in the case of elements whose salts are readily soluble or difficultly soluble, in which case naturally the potential of the electrode is affected as a result of the concentration of the solution.

We thus obtain the following series (upper) of the elements in the electropositive condition:

← (+)																			
Cs	Li	Ba	Mg	Zn	:	Hg	Tl	Pb	Bi	Sn	Sb	As	P	Te	Se	S	:	Strongly Negative	
Strongly Positive					:	Hg	Tl	Pb	Bi	Sn	Sb	As	P	Te	Se	S	:	I	O	Br	Cl	F
						Amphoteric Elements												(−) →				

Each element in this series is less electropositive than the preceding element, but all the elements in this series are electropositive with respect to strongly electronegative elements. On the other hand, certain elements appear in the electronegative condition, and we may construct a similar series of the elements with respect to their affinity for the negative charge. This series is the lower of the two given above. Ordinarily the only elements which are actually known in the electronegative condition

as ions are the halogens and the members of the sulfur group, sulfur, selenium and tellurium. However, as we shall see presently, the two series overlap, and many elements appear in both the positive and negative series as indicated. These may be termed amphoteric elements.[3]

By far the greater number of elements ordinarily exist in their compounds in an electropositive condition, while only a small number exist in the electronegative condition. From the standpoint of the constitution of the atom, we should expect a more nearly equal distribution between elements in the electronegative and the electropositive state. In general, those elements act electropositively which have a small number of electrons in the outer shell in excess of that required for stable configuration; while those elements act electronegatively which have a large number of electrons in the outer shell, and which reach a stable configuration by the addition of a small number of electrons. As we shall see presently, and as indicated above, actually a large number of the elements appear in an electronegative condition, but the nature of the compounds in which these elements appear in such a condition is obscured, owing to the properties of the compounds in question. In the first place, these compounds are reactive toward ordinary solvents; while, in the second place, a large number of these compounds are metallic.

It is commonly assumed that a compound which is metallic differs fundamentally in its constitution from a compound which is not metallic. Yet an examination of other properties of such compounds would scarcely bear out this view. If we consider, for example, the heats of formation of various compounds of the more electronegative elements with strongly electropositive elements, we find, for example, that the heat of formation diminishes quite regularly as we pass from the more electronegative to the less electronegative elements. For example, we have the following equivalent heats of formation of the more characteristically negative elements with a strongly electropositive element, calcium:

CaF_2	$CaCl_2$	$CaBr_2$	CaO	CaI_2	CaS	$CaSe$	CaH_2	Ca_3N_2	CaC_2
119.4	92.0	77.4	72.5	70.6	45.4	29.0	23.1	15.4	6.52

[3] Reichinstein, Z. f. phys. Chem., **97**, 257 (1921).

All the electronegative elements in this case are what are ordinarily considered as non-metallic elements. Let us examine the heats of formation of some characteristically metallic compounds. We have, for example, the following heats of formation in kilogram calories per mol:

$MgCd$	$NaCd_2$	$NaCd_5$	$NaHg$	$NaHg_2$	$CaZn_4$	Cu_2Cd_3	Mg_3Al_4	$MgZn_2$
17.7	30.8	60.6	10.3	17.8	55.6	47.7	164.8	24.9

Anyone who is familiar with the preparation of metallic compounds, such as the compounds of sodium with lead, tin, bismuth, antimony, mercury, etc., is well aware that the heat evolved in the formation of these compounds decreases as the less electropositive elements become more electropositive or, more correctly, less electronegative. The heats of formation of the compounds of tin are greater than those of lead, those of arsenic greater than those of bismuth, etc. The melting point curves of the compounds also clearly indicate varying degrees of stability of these compounds; thus, the melting point curves of sodium and mercury are relatively less steep than the corresponding curves of sodium and tin and sodium and lead; and still less so than those of sodium and bismuth or sodium and antimony. It would seem, therefore, that, so far as the formation of the compounds of strongly electropositive elements with electronegative elements is concerned, there is no break in the order of magnitude of the heat effect accompanying the formation of the compounds, as we pass from compounds which are non-metallic to compounds which are metallic. The very order of magnitude of the energy effects in the case of certain of these compounds leads us to infer that forces of an electrochemical nature must come into play here, for we know of no other forces sufficiently great to account for heat effects of the magnitude observed. As the electronegative constituent becomes less electronegative, the free energy of formation of the compound diminishes, but, in a condensed state, not all the electrons in the compound are held in fixed position, so that metallic properties appear. From what we know of the nature of metals, however, we should expect the metallic condition of these compounds to be restricted to the solid, or, rather, to the condensed state. If the distance between the molecules could be increased somewhat, the negative electrons,

without doubt, would combine with the atomic constituents from which they are derived, and the metallic properties would disappear. In other words, if we could discover a solvent in which these compounds were soluble, we should expect them to exhibit the properties of salts, in which the positive constituent would consist merely of the ion of the electropositive metal, and the negative constituent of the ion of the electronegative metal. We should not expect such solutions to exhibit metallic properties.

It is, of course, obvious that a solvent for any such compounds must be relatively inert; otherwise it will react with it. Let us consider, for example, a compound of sodium and tin, Na_4Sn. This reacts violently with water, with the evolution of hydrogen. The mechanism of this reaction is as follows:

$$Na_4Sn + 4HOH = 4NaOH + SnH_4,$$
$$SnH_4 = Sn + 2H_2.$$

In other words, the compound hydrolyzes, since stannane, H_4Sn, is an exceedingly weak acid. Furthermore, stannane is an unstable compound, which decomposes readily, so that under ordinary conditions it breaks down in the process of evolution and hydrogen is evolved with the precipitation of metallic tin. It is clear, however, that the mechanism of the reaction of compounds of this type with water is not one of direct reaction of the more electropositive metal with water, but an indirect reaction in which a hydride is formed. Indeed, by suitable means, the existence of the hydride may be established, and, in fact, has been so established.

The only solvent thus far discovered which is available for the solution of metallic compounds, as well as for certain of the metallic elements, is liquid ammonia. The alkali metals are readily soluble in liquid ammonia, forming solutions which exhibit markedly metallic properties. Furthermore, certain metallic compounds, namely the alkali metal salts of the hydrides of lead, tin, antimony, bismuth, arsenic, tellurium and selenium, are readily soluble in liquid ammonia, forming highly colored and rather opaque solutions, the color depending upon the nature of the metal. Thus, sodium-lead solutions are green, while the corresponding tin solutions are red.

These solutions have been investigated and it has been shown that they exhibit no metallic properties whatsoever.[4] On the other hand, they exhibit electrolytic properties analogous to those of ordinary salts. For example, solutions of compounds of sodium and lead, dissolved in liquid ammonia, conduct the electric current electrolytically. These compounds are formed comparatively readily, in liquid ammonia solution, through the direct interaction of the metals. Thus, if sodium is dissolved in liquid ammonia and a quantity of lead introduced, reaction takes place with the formation of a soluble sodium plumbide. When the ammonia is evaporated, the plumbide is left behind in metallic form.

As stated, the solutions of this type conduct the current with considerable ease. If, now, a current is passed though a solution, for example, of a compound of sodium and lead, between lead electrodes, it is to be expected that, if lead is the anion, it will be precipitated on the anode and dissolved at the cathode, and this, in fact, is what has been found to take place. A current passed between two lead electrodes leads to solution of lead at the cathode and precipitation of coherent metallic lead on the anode. This is of particular interest, inasmuch as metals in the electropositive condition, when precipitated from liquid ammonia solution, almost invariably appear in spongy form.

There is, however, one other property of these sodium-lead solutions which is of great interest and importance. If sodium is treated with lead in liquid ammonia, the blue color characteristic of sodium soon disappears, and a greenish or a greenish-black solution is formed. When the composition of this solution is examined, it is found that it varies, depending upon the length of time that the lead has remained in contact with the solution. If the lead is left in contact with the solution for a sufficient length of time, the solution finally reaches an equilibrium condition, in which 2.25 atoms of lead are associated with an atom of sodium, which corresponds to a compound of the formula Na_4Pb_9. This proportion of sodium and lead in these solutions is in fact independent of concentration.

Obviously, if we wish to precipitate lead on a lead anode, from

[4] Even very concentrated solutions of sodium-lead compounds in liquid ammonia, which have a lustrous metallic appearance, conduct the current electrolytically.

a solution of a lead compound in liquid ammonia, it is necessary for the solution to be in equilibrium with free lead. If a solution containing a compound Na_4Pb_9 is electrolyzed, we obtain precipitated on the anode, not 0.5 atom of lead per equivalent of electricity, as in the case of plumbous nitrate, for example, but 2.25 atoms of lead for every equivalent of electricity passing through the solution. This indicates, then, that we have present in the solution a complex anion, which, in all likelihood, carries 4 negative charges and comprises altogether 9 lead atoms.

It may at first appear singular that lead should form an anion of this degree of complexity. A more careful examination of the properties of the elements in the electronegative condition, however, leads us to the conclusion that this is a general property of elements in this state. Heretofore, this property has been observed only in the case of a few of the most strongly electronegative elements, because of the fact that compounds of the less electronegative elements are not soluble in water (or react with it), and are not soluble in other common solvents.

I may call attention to the fact that iodine forms a complex anion I_3^- in aqueous solution, and it is known that under suitable conditions compounds may be obtained whose iodine content runs as high as KI_7. We have similar compounds in the case of the complex sulfides. Sulfides have been prepared in aqueous solution with a composition ranging from Na_2S to Na_2S_5, and in non-aqueous solutions compounds may be obtained with an even higher content of sulfur. It is known, too, that selenium and tellurium form complex anions, although these have not been studied extensively in aqueous solution.

Oxygen, under certain conditions, forms complex oxides. So we have, for example, the oxides K_2O, K_2O_2, K_2O_4, and, very likely, K_2O_3. When we come to examine the compounds of the less electropositive, that is to say, of the electronegative elements in liquid ammonia solution, we find that the elements of the 6th, 5th and 4th groups, particularly the heavier elements, all form salts with complex anions, which are comparatively soluble. For example, Peck has studied the solutions of sodium-antimony compounds in ammonia, and found that the ratio of antimony to sodium varies as a function of the concentration with a maxi-

mum ratio corresponding to the formula Na_3Sb_7.[5] In liquid ammonia we have complex tellurides, corresponding to the formulæ Na_2Te_2 and Na_2Te_4. It has been shown that the tellurium anion carries two charges. Like lead, antimony may be precipitated on an anode, and the same is true of other elements.

What appeared as an exceptional property in the case of lead, in the first place, has turned out to be a general property of a large number of elements. There are indications that sodium thallide is very slightly soluble in liquid ammonia; but apparently other compounds of elements of the 3rd and 2nd groups are insoluble in liquid ammonia.

One of the striking properties of the inter-metallic compounds, and one which has presented the greatest difficulties in the way of explanation, is the multiplicity of compounds derivable from a single pair of metallic elements. The ratio of the atoms of metallic elements combining with one another appears to bear no relation whatsoever to the usual valence of the elements in their ordinary compounds. Yet these compounds are stable and well defined. In the case of sodium and lead we may form a series of compounds, all of which are soluble in liquid ammonia, but none of which is stable in the presence of free lead, excepting the compound Na_4Pb_9. It may be inferred, therefore, that just as lead, antimony and bismuth form complex anions, other of the metals likewise form complex anions, which serves to account in large measure for many compounds, which a given pair of elements may form, and for the lack of apparent regularity of the ratios in which the elements combine.

The values of the free energy of formation of many metallic compounds, that is, compounds between strongly electropositive elements and elements which are weakly electronegative, indicate by their magnitude that the forces involved are of the same nature as those acting in the case of ordinary salts. For example, the free energy of formation of a number of metallic compounds[6] per atom of the electropositive metal follows:

$NaSn_x$	$NaSb_x$	$NaPb_x$	$NaTe_{x\,sol.}$	$NaBi_x$	$CaSb_x$
39700	43000	39100	49900	44200	37000
ZnSb	$NaHg_5$	$LiHg_3$	KHg_{12}	$RbHg_{12}$	
24800	18350	22080	24920	25520	

[5] Jour. Am. Chem. Soc., 40, 335 (1918).

[6] The first seven of these were determined by Dr. Earle F. Whyte in the author's laboratory. For the remainder *cf.* Gerke, J. Am. Chem. Soc., 45, 2507 (1923).

The order of magnitude of the energy effects, and the order in which the elements appear in this series, agree with the assumption that these substances are saltlike or ionic in their constitution. Excepting in the case of mercury, the precise composition of the compound formed is not known. In the case of the more electronegative elements, at any rate, the formation of the more complex compounds from the less complex compounds is probably not accompanied by a great energy change. Nevertheless, in many instances, certain compounds of intermediate complexity are doubtless more stable than compounds of greater or lesser complexity. Thus, the hydrargide $NaHg_2$ is more stable than NaHg or Na_2Hg, since, in the presence of ammonia, transformation takes place to $NaHg_2$, with the formation of free metallic sodium in ammonia solution. Similar reactions take place in the case of solutions of plumbides rich in sodium in liquid ammonia. This is a very interesting case of reduction.

The solutions of metallic compounds in liquid ammonia exhibit chemical properties similar to those of ordinary salts. Ionic reactions occur in which the less soluble constituent is precipitated, as, for example, in the case of the complex tellurides. On treating sodium telluride with a calcium salt, calcium telluride is precipitated and the sodium salt remains behind. Provided the compounds of the various ionic constituents are all soluble, no reaction occurs between these compounds and ordinary salts. An interesting case arises when, for example, a solution of a lead salt, in which a positive lead ion occurs, is added to a solution of a lead salt with a negative lead ion. In this case we have the reaction:

$$2Pb^{++} + Pb_9^{----} = Pb_2.Pb_9$$

In other words, a positive lead ion combines with a negative lead ion, or, at any rate, neutralizes a negative lead ion, with the formation of free metallic lead.

Electrochemical reactions take place between the elements in the electronegative condition, and solutions of other elements in the same condition. Thus tellurium displaces antimony and tin displaces lead from its solutions. It would appear that tin is markedly more electronegative than lead.[7] Lead in the crystal-

[7] Observations by Dr. F. W. Bergstrom in the author's laboratory.

line form may be obtained by introducing metallic tin into a solution of sodium plumbide. Similar oxidations may, of course, be carried out by the introduction of still more electronegative elements.

Another very interesting series of reactions is found in the action of liquid ammonia solutions of certain electrolytes on various elements. These reactions are, of course, greatly influenced by the properties of the compounds formed; more particularly, their solubility. Potassium amide is the most interesting electrolyte for the study of reactions of this type. If various elements are treated with potassium amide, two types of reactions occur, depending upon the electropositiveness of the metal in question.[8] If the metal is not markedly electronegative, then the reaction which occurs will be one of replacement of potassium by the metal in question, with the formation of free potassium and an ammono-salt of the metal, according to the equation:

$$M^n + nKNH_2 = nK + M(NH_2)_n$$

the amphoteric base, $M(NH_2)_n$, reacting with the strong base, KNH_2, to form an ammono-salt. Potassium is also readily reduced from its halides by means of metallic calcium or even magnesium, reaction taking place according to the equation:

$$2KCl + Ca = CaCl_2 + 2K$$

This is, in fact, a simple metathetic reaction. In the case of potassium amide, reduction takes place even with much less electropositive elements, because of the fact that the resulting amphoteric amide reacts with potassium amide to form an ammono-basic potassium salt, which keeps down the concentration of the positive ions of the metal in question. For example, potassium is reduced from potassium amide by means of metallic aluminum, although the difference in potential of aluminum and potassium in the potential series is in the neighborhood of several volts.

These reactions suggest an explanation for the action of the alkalies on certain metals in aqueous solution; for example, the action of potassium hydroxide on aluminum. As is known, potassium hydroxide reacts readily with aluminum with the formation of an aluminate and hydrogen. The concentration of hydrogen

[8] From observations by Dr. F. W. Bergstrom in the author's laboratory, many of which remain to be published. See also Jour. Am. Chem. Soc., **45**, 2788 (1923).

ions in a strong potassium hydroxide solution is certainly too low to account for this reaction, and it is not to be expected that aluminum reacts directly with water. On the other hand, aluminum in water, as in ammonia, tends to react with a base, with the formation of free potassium and a potassium aluminate. In the case of water, of course, the free potassium reacts immediately with the solvent to regenerate the hydroxide with the evolution of hydrogen. The action of the hydroxides on zinc may be similarly accounted for.

The action of potassium amide on the more electronegative metallic elements is interesting. We have only a few reactions in aqueous solution which may serve as analogues. For example, potassium hydroxide reacts with chlorine with the initial formation of potassium chloride and potassium hypochlorite. In other words, in this reaction one atom of chlorine may be looked upon as acting electropositively in the hypochlorite, and another electronegatively in the chloride.

In the case of solutions in liquid ammonia, the action of potassium amide has been studied on the whole series of negative elements as far as thallium and zinc.[9] With all the elements as far as lead, at any rate, reaction takes place according to the equation:

$$(1 + \frac{m}{n})\ M + mKNH_2 = \frac{m}{n}\ M(NH_2)_n + K_mM,$$

m being the negative and n the positive valence of the atom M. To take a specific example, metallic tin reacts with potassium amide according to the equation:

$$3Sn + 4KNH_2 = K_4Sn + 2Sn(NH_2)_2,$$

the amphoteric ammono-base $Sn(NH_2)_2$ reacting further with KNH_2 to form an ammono-salt. With other elements, such as antimony, bismuth, sulfur, tellurium, and the like, similar reactions occur.

It may be pointed out that reactions of this type likewise take place in aqueous solution. For example, the action of potassium hydroxide on tin with the evolution of hydrogen takes place according to a corresponding equation. In most of these reac-

[9] Observations by Dr. F. W. Bergstrom in the author's laboratory.

tions there is formed hydrogen, together with a salt of an aquo-acid. This is due to the fact that the salt K_nM, which is formed, is hydrolyzed by water to form the acid H_nM, which decomposes with the evolution of hydrogen. When, for example, potassium hydroxide acts on tin with the evolution of hydrogen, the reaction takes place according to the equations:

$$3Sn + 4KOH = 2Sn(OH)_2 + K_4Sn$$
$$K_4Sn + 4H_2O = 4KOH + H_4Sn$$
$$H_4Sn = 2H_2 + Sn$$

We thus see that the physical properties of the compounds of metallic elements, as well as the reactions of these compounds in ammonia solution, give unquestioned evidence of the existence of metallic elements in an electronegative condition. We see further that the reason why the existence of the elements in this condition has not been heretofore recognized, is due to the fact that the compounds of these elements are not, in general, stable in aqueous solution. However, certain reactions in aqueous solution, which otherwise are not readily accounted for, are readily understandable in the light of our knowledge of the behavior of these compounds in solutions in liquid ammonia.

Excepting the strongly electropositive and the strongly electronegative elements, all elements exhibit amphoteric properties, in that they act electropositively in the presence of more electronegative elements and electronegatively in the presence of more electropositive elements. Most of the elements occupying an intermediate position in the series of electro-affinities are metallic, and form metallic compounds with many other elements. The condition of metallicity, however, is largely incidental, and is restricted to compounds in the condensed state. In solution, the compounds exhibit electrolytic properties; thus showing that they do not differ in constitution from ordinary salts. It is a characteristic property of the simple anions of these elements to form complex anions by reaction with the free elements. This property serves to account for the multiplicity of compounds formed between a given pair of metallic elements.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

RECENT PROGRESS IN ELECTROPLATING AND ELECTROFORMING.[1]

By W. Blum[2].

In this brief review of the developments of interest to the electroplating and electroforming industries during the post-war period, no attempt will be made to include an exhaustive bibliography or discuss critically the individual researches. Instead, an effort will be made to point out the relations and possible significance of such work as has been completed or is in progress. The recent activities may for convenience be considered under the following headings, which, however, are not sharply defined, *viz.*, (1) Research on the principles and theories of electrodeposition; (2) Research upon the deposition of specific metals; (3) Literature reviews and pedagogical activities, and (4) Changes in electroplating practice.

I. PRINCIPLES OF ELECTRODEPOSITION.

Much further research and thought will be required before a theory is developed by which the existing data of electrodeposition can be correlated, and from which new facts can be predicted. Until such a goal is approached, the literature of electrodeposition will contain many apparently contradictory statements, and research will of necessity be largely empirical. The most promising feature of the progress in recent years is that numerous investigators have sought to co-ordinate the results of specific researches and observations, in the effort to develop at least a working hypothesis upon which ultimately a comprehensive theory of electrodeposition can be constructed. Among those who, with their associates, have in recent years contributed to the theory of

[1] Published by permission of the Director of the Bureau of Standards. Manuscript received February 28, 1924.

[2] Chemist, Bureau of Standards, Washington, D. C.

electrodeposition may be mentioned Aten[3], Hughes[4], Kohlschütter[5] and Blum.[6]

The structure of electrodeposited metals is of paramount importance, because it determines their properties. Most of the papers just mentioned relate directly to the structure. In addition, reference should be made to the recent work upon the relation between the structure of a base metal and that of the deposit made upon it.[7] More extended investigation will be required before the practical significance of such behavior in commercial practice can be determined. It presents a fascinating field for metallographic study. The diffusion of electrodeposited metals into zinc[8] is an instance of an effect of the base metal upon the deposit subsequent to deposition.

Among the researches relating to general principles, may be mentioned the studies on overvoltage[9] by Tainton, Goodwin, Knobel and their associates. Such work is essential to a proper understanding of the significance of electrolytic potentials, especially those observed during the deposition of metals less noble than hydrogen, such as nickel, iron and zinc.

A much discussed property of electroplating baths is the "throwing power" or ability to deposit metal uniformly upon irregularly shaped articles. Heatley[10] has given a mathematical analysis of the current distribution in multiple electrode systems, and has pointed out its possible application to electrodeposition. Haring and Blum[11] have defined this property in simple terms and have devised an apparatus by which the relative throwing powers of different solutions may be readily measured. Incidental to such measurements, interesting data upon the potential relations during electrolysis were obtained.

[3] A. H. W. Aten and Louise Boerlage, Rec. Trav. Chim. Pay-Bas, **39**, 720 (1920).
[4] W. E. Hughes, Bull. 6, Dept. Sci. and Ind. Res., London (1922) and Beama, **12**, 215 (1923).
[5] V. Kohlschütter and E. Vuilleumier, Z. Elektrochemie, **24**, 300 (1918) and H. Stäger, Helv. Chim. Acta, **3**, 584 (1920).
[6] W. Blum and H. S. Rawdon, Trans. Am. Electrochem. Soc. **44**, 397 (1923).
[7] W. Blum and H. S. Rawdon, Trans. Am. Electrochem. Soc. **44**, 305, (1923), and A. K. Graham, Trans. Am. Electrochem. Soc. **44**, 427 (1923).
[8] W. G. Traub, Trans. Am. Electrochem. Soc. **42**, 55 (1922).
[9] U. C. Tainton, Trans. Am. Electrochem. Soc., **41**, 389 (1922).
H. M. Goodwin and M. Knobel, Trans. Am. Electrochem. Soc., **37**, 617 (1920).
H. M. Goodwin and L. A. Wilson, Trans. Am. Electrochem. Soc., **40**, 173 (1921).
M. Knobel, P. Caplan, and M. Eiseman, Trans. Am. Electrochem. Soc., **43**, 55 (1923).
M. Knobel and D. B. Joy, Trans. Am. Electrochem. Soc., **44**, 443 (1923).
[10] A. H. Heatley, Trans. Am. Electrochem. Soc. **44**, 283 (1923).
[11] H. E. Haring and W. Blum, Trans. Am. Electrochem. Soc., **44**, 313 (1923).

II. RESEARCHES ON SPECIFIC METALS.

This work may be divided into the studies upon the metals and baths in common use, and upon those which are considered rare or uncommon in this connection. However, no such sharp distinction can be made. Thus, the commercial electrodeposition of iron was, until recent years, unusual. Later work[12] has however shown that it is an entirely practicable process, and may find numerous applications, such as in building up worn parts, and in the electroforming of tubes[13], etc.

The great value of symposia in bringing together existing knowledge and stimulating research and experiment, is illustrated by the collection of papers on silver plating[14] before the Faraday Society in 1921.

In a study of nickel deposition Thompson[15] has shown the significance of the acidity of the solutions, and has described methods for its measurement in terms of the pH system, now almost universally adopted by biological and physical chemists for expressing hydrogen ion concentration. The effects of impurities such as copper, zinc and iron in nickel baths have also been determined.[16] Other studies at the Bureau of Standards have included the conductivity of nickel solutions, and the properties and behavior of nickel anodes.

The paper by C. P. Madsen[17] upon ductile nickel is of special interest in electroforming. The work of Graham[18] upon the nickel plating of zinc suggests new methods for attacking this important problem.

[12] W. A. MacFayden, Trans. Far. Soc. **15**, 98 (1920).
W. E. Hughes, Dept. Sci. and Ind. Res. London, Bull. 6, 1922; Chem. and Met. Eng. 26, 267 (1922).
D. R. Kellogg, Preprint Am. Inst. Min. and Met. Eng., Feb., 1922.
J. D. Alley, Machinery, **30**, 202 (1923).
N. B. Pilling, Trans. Am. Electrochem. Soc. **42**, 9 (1922).
H. D. Hineline, Trans. Am. Electrochem. Soc. **43**, 119 (1923).
B. H. Thomas, Automotive Ind. **43**, 418 (1920).

[13] B. Stoughton, Chem. and Met. Eng., **26**, 128 (1922).

[14] Barclay, W. R., Electrosilver plating, Trans. Far. Soc., **16**, 515 (1921).
Brook, G. B., and Holmes. L. W., The Chemical Composition of Old Silver Plating Solutions, Trans. Far. Soc., **16**, 524, (1921).
Mason, F., A New Maximum Current Density in Commercial Silver Plating, Trans. Far. Soc., **16**, 534, (1921).
Brook, I. B., The Crystalline Structure of Electrodeposited Silver, Trans. Far. Soc., **16**, 538 (1921).

[15] M. R. Thompson, Trans. Am. Electrochem. Soc., **41**, 333, (1922).

[16] M. R. Thompson and C. T. Thomas, Trans. Am. Electrochem. Soc., **42**, 79 (1922).
M. R. Thompson, Trans. Am. Electrochem. Soc., **44**, 359 (1923).

[17] C. P. Madsen, Trans. Am. Electrochem. Soc., **39**, 269 (1921).

[18] A. K. Graham, Trans. Am. Electrochem. Soc. **44**, 347 (1923).

Interest in zinc plating has been greatly increased because of its recognized value for protection against the corrosion of iron and steel. Recent researches[19] have related chiefly to the zinc cyanide plating solutions, principally because of their generally recognized superior throwing power. The obvious advantage in cost, simplicity and stability which are possessed by the acidified zinc sulfate baths emphasize the desirability of improving their throwing power. If this can be made to approach that of the cyanide solutions, a great impetus will be given to the use of the sulfate baths.

A few papers have appeared in recent years upon lead[20] and tin[21] plating, although neither process is extensively applied commercially.

One of the less common metals recently employed in electroplating is cadmium. Although no extended researches upon this subject have been published, the process has been applied to a considerable extent upon a commercial scale. Cadmium exerts intrinsic protection to small exposed areas of iron and steel, and is not itself so readily corroded as zinc. The probable field for cadmium plating therefore lies in the protection of iron by a metal which is in many properties intermediate between zinc and nickel. Further observation will be required to determine whether its use as a protective coating under different conditions of exposure is warranted by its increased cost.

The outstanding new subject of research in electrodeposition in the last few years is chromium plating. Owing to the fact that many of the published references to such work are vague or incomplete, it is difficult to summarize the results. So far as can be learned, it appears that the deposition of chromium in a coherent and adherent form is entirely feasible, and that the difficulties which now hinder its commercial application are no more insuperable than those which have been overcome with other metals. The commercial field for chromium plating remains to be defined. Its chief value appears to depend upon the great resistance of chromium to oxidation at elevated temperatures, and to atmospheric and chemical attack, and upon the fact that the chro-

[19] C. J. Wernlund, Trans. Am. Electrochem. Soc., 40, 257 (1921); W. G. Horsch and T. Fuwa, Trans. Am. Electrochem. Soc., 41, 389 (1922).

[20] F. C. Mathers, Trans. Am. Electrochem. Soc., 38, 121 (1920).

[21] F. C. Mathers and W. H. Bell, Trans. Am. Electrochem. Soc., 38, 135 (1920).

mium deposits are more nearly impervious than are those of most metals. This property is of special importance, if, as now appears probable, the chromium coating will not protect adjacent small exposed areas of the underlying iron. The principal recent publications on this subject are those of Sargent,[22] Liebreich[23] and Schwartz.[24]

The deposition of alloys is of importance, both with respect to their intentional production, when they are desired, and their avoidance when pure deposits are essential. There is no other single branch of electrodeposition in which there are so many important and fascinating problems as in the deposition of alloys. Brass plating is now conducted commercially upon a large scale, and appropriately therefore we find that the most extensive recent work on alloy deposition is devoted to brass plating[25]. Bronze plating[26] has also been studied but is not employed on a commercial scale. The study of the deposition of lead-tin alloys[27] is of interest chiefly in illustrating certain principles and methods of study.

III. REVIEWS AND PEDAGOGICAL ACTIVITIES.

Even more significant than the researches in recent years are the summaries of the literature of electrodeposition. Especially in the present state of the electroplating industry it may be even more important to render conveniently available that which has been learned by research and experience than to add to our existing store of knowledge. A splendid illustration of such activities is the comprehensive resumé upon iron deposition by W. E. Hughes.[28] The same author[29] has published in simple readable form a series of articles upon the plating of the various metals, and more recently[30] has reviewed critically the work done in electrodeposition in the past two years. Knox[31] has also published

[22] G. J. Sargent, Trans. Am. Electrochem. Soc. **37**, 479 (1920).
[23] E. Liebreich, Z. Metallkunde, **14**, 367 (1922); Z. Elektrochemie **29**, 208 (1923).
[24] K. W. Schwartz, Trans. Am. Electrochem. Soc. **44**, 451 (1923).
[25] A. L. Ferguson and E. G. Sturdevant, Trans. Am. Electrochem. Soc., **38**, 167 (1920).
[26] F. C. Mathers and S. Sowder, Trans. Am. Electrochem. Soc., **37**, 525 (1920).
[27] W. Blum and H. E. Haring, Trans. Am. Electrochem. Soc., **40**, 287 (1921).
[28] Trans. Am. Electrochem. Soc., **40**, 15 (1921).
[29] Beama, **6**, 415 (1920); **7**, 101 (1920); **8**, 133, 239, 425 (1921); **9**, 137, 335, 555, (1921); **10**, 138 (1922); **12**, 19, 92 (1923).
[30] W. E. Hughes, Electrician, **41**, 628 (1923).
[31] W. G. Knox, Metal Industry, **17**, 269, 372 (1919); **18**, 14, 168, 264, 361, 556 (1920); **19**, 25, 160, 336 (1921).

a number of papers upon the deposition of the important metals. Haas[32] has summarized the existing knowledge and practice in nickel plating.

The American Electroplaters' Society has in its Monthly Review published numerous articles upon plating practice, which are suggestive and stimulating both to platers and investigators. To this Society should be given a large share of the credit for the increased interest in this field recently developed in the American Electrochemical Society.

IV. PLATING PRACTICE.

Frequently we realize keenly the gap that exists between the acquisition of knowledge and its practical application in an industry. That such a gap still exists in the electroplating field cannot be denied, but fortunately it is being bridged by the co-operation of electroplaters and chemists, of which co-operation there are many encouraging evidences. It is probable that there are today in America ten times as many chemists who are directly interested in electroplating, as there were ten years ago, and, what is even more significant, there are many more platers who have acquired a working knowledge of chemical principles. The result of the co-operation between chemists and electroplaters is indicated by the increasing number of plants in which solutions are operated under analytical control, by the more frequent use of devices for agitation, filtration, circulation and mechanical operation, by the efforts to apply both new and old principles to practical problems, and by the more frequent use of specifications for plating. Such a result has been accomplished only because chemists have recognized that the platers have through long experience gained a large fund of information, and that the two groups working together can accomplish that which neither can do separately. The Electrochemical Society should continue its efforts to foster just such co-operation, through appropriate symposia and round table discussions.

[32] J. Haas, Jr., Metal Ind., **19**, 364 (1921); **20**, 430 (1922); **21**, 64, 230, 273, 484 (1923); **22**, 18 (1924).

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

NICKEL ANODES FOR ELECTROPLATING.[1]

By C. T. Thomas[2] and W. Blum.[3]

Abstract.

The anode current efficiency, anode potential and character of anode corrosion were determined for about twenty nickel anodes, representing the various types of nickel available for this purpose. The relation of the composition, structure and method of preparation to the behavior of the anodes is pointed out.

I. INTRODUCTION.

This study of the behavior of nickel anodes constitutes one phase of a general research upon nickel deposition in progress at the Bureau of Standards. A survey of the literature showed that there are at present very few quantitative data from which the behavior of nickel anodes may be predicted, or upon which reasonable specifications for commercial nickel anodes may be based. That there is a need for such information is evident from the great diversity of opinion and practice upon the best type of nickel anodes for use in electroplating and electroforming.

The present research represents a general survey of the field, from which the effects and relations of those factors which appear most important have been determined. Much more comprehensive researches will be required in order to explain and co-ordinate many of the observed phenomena, and more extensive observations in commercial plants will be needed before complete specifications for the manufacture and use of nickel anodes can be satisfactorily defined. As it is not feasible to extend this study at

[1] Published by permission of the Director of the Bureau of Standards, Department of Commerce. Manuscript received February 19, 1924.

[2] Assistant Chemist, Bureau of Standards, Washington, D. C.

[3] Chemist, Bureau of Standards, Washington, D. C.

the Bureau in the near future, the results are published for the benefit of those who may desire to conduct further investigations.

II. LITERATURE.

Notwithstanding the numerous publications upon the passivity of nickel, which is an underlying factor in the behavior of nickel anodes, few published papers contain direct references to the use of nickel anodes in nickel solutions. The relation of passivity to the problem is discussed by E. P. Schoch,[4] who did not, however, make determinations of anode efficiency. The only recorded quantitative measurements of anode efficiency that could be found are those of O. W. Brown[5] and L. D. Hammond,[6] each of whom made such measurements upon a small number of anodes from their loss in weight. Other published articles relating to nickel anodes usually consider their manufacture and general behavior and the loss of metal in slime and scale arising during their use.

III. SCOPE OF INVESTIGATION.

Before deciding which factors are most likely to have significant effects upon the behavior of nickel anodes, it is necessary to decide what constitutes a satisfactory anode. The requirements to be met or approximated may be briefly summarized as follows:

It should corrode uniformly, with low polarization and with a high anode current efficiency, and should not introduce any deleterious substances into the solution. If the corrosion is not uniform, small particles may become detached and carried to the cathode and there cause roughness, or large masses may drop off and cause waste. If the anode efficiency is not high, or at least nearly equal to the cathode efficiency, the metal content of the solution will decrease and the solution will become more acid (the pH will decrease).

The primary consideration in electrodeposition is the quality of the metallic deposit, and hence the relation of the anode behavior to the properties of the cathode is of paramount importance. Such a relation is involved even though not stated

[4] "Behavior of the Nickel Anode and the Phenomena of Passivity," Am. Chem. J. 41, 232 (1909).

[5] "Efficiency of the Nickel Plating Tank," Trans. Am. Electrochem. Soc. 4, 83 (1903).

[6] "The Electrodeposition of Nickel," Trans. Am. Electrochem. Soc., 30, 103 (1916).

in the above mentioned criteria. *A change in the behavior of an anode cannot exert any effect upon the properties of the cathode except by forming suspended particles or by producing changes in the solution,* which in turn influence the cathode behavior.

In order to obtain definite data from which the behavior of nickel anodes might be defined, about twenty anodes were secured or prepared, representing the four principal types of nickel, *viz.*, electrolytic, rolled, cast, and shot; with certain variations in the composition or method of preparation. The microstructures were photographed, and the anode efficiencies and electrolytic potentials during electrolysis were measured in various types of solutions. The behavior of the anodes during electrolysis was observed and any marked indirect effects upon the cathode deposit were noted.

TABLE I.

Percentage Composition of Typical Commercial Cast Nickel Anodes.

	1	2	3	4	5	6	7	8	9*
Nickel + Cobalt ..	98 0	97 5	97 7	97 2	97.3	97 0	96.9	95.0	91 8
Iron.....	0.56	0.60	0.90	0 55	1.18	0.61	0.78	2.64	6.41
Copper	0 24	0.20	0.15	0.12	0.26	0.16	0.19	0.54	0.26
Carbon	1.09	1.50	0.81	1.26	0.73	1.63	1.58	0 65	1.20
Silicon	0.08	0.05	0.24	0 18	0.38	0 23	0.24	0.42	0.22
Manganese ..	.....	.....	.....	.....	.....	.....	0.16	0.03	.....
Tin	.....	.....	....	0 60	.....	....	....	0 60	..
Total.....	99 97	99.85	99 70	99 91	99 85	99 63	99 85	99 88	99 89

* No. 9 was purchased as 90-92 per cent, all others as 95-97 per cent nickel anodes.

IV. MATERIALS USED.

Anodes. In Table I are shown the compositions of a number of commercial cast nickel anodes which have been analyzed at the Bureau of Standards in recent years.

It may be seen that all of these anodes contained appreciable but variable amounts of carbon, iron, copper and silicon. At the time when these anodes were analyzed, it was not possible to co-

ordinate their behavior with their chemical composition, although it may be significant that the only two (No. 5 and 8) which were known to be unsatisfactory had a low carbon content.

Table II records the characteristics of the anodes used in this investigation.

TABLE II.

Nickel Anodes Employed in this Investigation.

Anode No.	Type	Composition, Per Cent							
		C	Fe	Si	Cu	Sn	S	Mg	Mn
1	Electrolytic	0.02	0.13		0.30				
2	Hot rolled*	0.13	0.56	0.03	0 14		0.03		0.14
3	Chill cast†	0.01	0.45		0.26		0.04		
4	Sand cast	0.12							
5	Chill cast	0.37							
6	Sand cast	0.35							
7	Chill cast	1.43							
8	Sand cast	1.38							
9	Sand cast‡	0.5					0.15		
10	Sand cast‡	0.5					0.17	0.17	
11	Sand cast‡	1.5					0.16		
12	Sand cast‡	1.5					0.10	0.22	
13	Sand cast	0.12	1.45						
14	Sand cast‡	1.5	1.45						
15	Sand cast‡	1.0	5.7						
16	Sand cast‡	1.5		1.59					
17	Sand cast‡	1.5			1.0				
18	Sand cast‡	1.5				1.0			
19	A Shot¶	0 12	0.39	0.10	0 16		0 03		
20	M Shot§	0 06	0.06		0.03				

* A portion of a 1 in. hot rolled nickel bar.

† Refined nickel, for use as anodes, melted on a large scale without deoxidation. Contains about 0.5 per cent NiO.

‡ Carbon content estimated from amount introduced.

¶ Poured shot.

§ Carbonyl shot, produced by the decomposition of nickel carbonyl, in the Mond process.

The electrolytic, rolled and shot anodes represented commercial materials furnished to this Bureau for use in this study. Most of the cast anodes were prepared at this Bureau from electrolytic nickel, to which appropriate additions were made. The metal was melted in "plumbago" crucibles, the requisite amount of carbon was added in the form of charcoal, and other constituents in

appropriate forms. The chill castings were made in split steel molds, and the sand castings in dry sand molds.

The compositions stated in Table II are, unless otherwise noted, based upon actual analyses, and therefore vary slightly from the concentrations intended. Such variations are however no greater than are likely to occur in commercial practice. In most cases only the content of the added constituent was determined, as a complete analysis was unnecessary in those cases where the anodes were prepared from the same lot of nickel.

The microstructures of all these anodes were observed and recorded. A few of the most typical and significant structures are shown in Fig. 1 and 2. For general etching the specimens were treated with a reagent[7] consisting of

	Parts by Vol.
Glacial acetic acid	3
Concentrated nitric acid	3
Water	4

which required in some cases as much as one hour for satisfactory etching. For deep or contrast etching the specimens were etched electrolytically as anodes in hydrochloric acid (1-1) at a high current density for the necessary period, which varied from 10 sec. to 5 min. The possible relation of the structures to the behavior of the anodes is discussed later in this paper.

Solutions. The principal solutions used in the experiments are listed in Table III. The compositions were selected as representative of the types of solutions in commercial use in this country, but are not necessarily recommended for any specific purpose.

A few preliminary experiments with solutions similar to No. 1, but containing sodium chloride instead of ammonium chloride, showed that practically coincident results were obtained. The results obtained in a few tests with solutions containing sodium fluoride (0.25 *N*) in place of the chloride, will be referred to later.

V. METHODS OF STUDY.

Anode Efficiency. Before devising a procedure to measure anode current efficiency it is necessary to define it. In general it may be defined for a pure metal as the ratio of the weight of

[7] Circular 100, U. S. Bureau of Standards.

metal dissolved from the anode by the passage of a given quantity of electricity, to the maximum weight that could be dissolved by that quantity of electricity in accordance with Faraday's Law. Since, however, nickel anodes usually contain appreciable amounts of other elements, some of which may be dissolved electrochemically, it is necessary to decide arbitrarily what basis to use in expressing the anode efficiency. As iron is present in almost all nickel anodes, and as appreciable amounts pass into the

TABLE III.

Solutions Used.

Solution No.	Type	Constituents	Concentrations		
			N	g./L.	oz./gal.
1	Chloride	$NiSO_4.7H_2O$	1.00	140	19
		NH_4Cl	0.25	13	1.8
		H_3BO_3	0.25 (M)†	15.5	2.1
2	Double salt*	$NiSO_4.7H_2O$	1.00	140	19
		$(NH_4)_2SO_4$	0.25	16.5	2.2
		H_3BO_3	0.25 (M)†	15.5	2.1
3	Single salt	$NiSO_4.7H_2O$	1.00	140	19
		H_3BO_3	0.25 (M)†	15.5	2.1

* Equivalent to 50 g./L. (6.7 oz./gal.) of $NiSO_4.(NH_4)_2SO_4.6H_2O$ plus 105 g./L. (14 oz./gal.) of $NiSO_4.7H_2O$.

† Molar concentrations.

deposits without necessarily detrimental effects, it is most convenient to define the anode efficiency in terms of the nickel[8] plus iron, which are dissolved from the anode.

Reliable results cannot be obtained from the loss in weight of the anodes, owing to (a) mechanical losses and (b) absorption of the electrolyte in the pores of the anode. It was therefore found necessary to compute the anode efficiency in each case from a "nickel (plus iron) balance", that is, the amount of nickel and iron dissolved from the anode is equal to the algebraic sum of the nickel and iron deposited upon the cathode, the change in the

[8] Throughout in these experiments, no attempt was made to differentiate between the nickel and cobalt in the anodes. It is probable that most of the anodes used contained small amounts of cobalt, say from 0.5 to 1.0 per cent Co.

nickel and iron content of the solution and the nickel and iron contained in that portion of the sludge which was precipitated during the electrolysis. This method involves a considerable number of analyses for each determination, and appears somewhat complicated. No other procedure tried was found to give uniformly accurate results.

For measuring the anode efficiency, a number (usually four) of the anodes were operated in series in separate beakers. The anodes were in the form of cylinders 2.5 x 10 cm. (1 x 4 in.) which were immersed in the solution to a depth of 8 cm. (3.2 in.), giving an exposed anode area of about 67 sq. cm. (11 sq. in.), which area was used in computing the current densities. No allowance was made for the change in area during the course of the limited number of experiments, as the apparent decrease in area was usually at least in part counterbalanced by the increase due to roughening of the surface.

A plate of electrolytic nickel was bent to form a cylinder of approximately the same size as the other anodes. The nickel shot were contained in a perforated hard rubber cylinder of this same size inside. It was impracticable to compute the actual or effective area of the shot used in an experiment, and the current densities given for them are based arbitrarily upon the inside area of the cylinder in which they were contained. It was observed that most of the corrosion of the shot occurred on the outer layers of the shot adjacent to the holes in the container.

The cathode in each case consisted of a brass strip 10 x 30 cm. (4 x 12 in.) bent into a cylinder, which fitted into the glass beaker. The anode was attached to a vertical shaft which was rotated at 75 r. p. m., in order to insure mixing of the solution. Without such agitation, the solution stratified into layers of different composition and acidity, in which of course the anode corrosion would not be uniform. By rotating the anodes a nearly clean surface was maintained. The results therefore represent the relative behavior of clean anodes and not of those coated with sludge, such as is often present on anodes used in still baths. It was not possible, however, to obtain reproducible results with coated anodes. By the concentric arrangement of the anode and cathode,

a uniform current density was maintained on each, although the current density on the cathode was only about 20 per cent of that on the anode.

Before each run the anode, cathode and beaker were moistened with the solution to be used in order to compensate for the volume of the solution adhering to them at the end of a run. A measured volume (600 cc.) of the filtered solution was then introduced. At the end of a run, in each of which a total current of about 9 ampere hours per square decimeter was passed, (*i. e.,* for 18 hr. at 0.5 amp./sq. dm. or 6 hr. at 1.5 amp./sq. dm.) the solution was withdrawn and diluted to 600 cc., to replace the loss by evaporation. A copper coulometer was run in series with the baths containing the anodes in order to measure the quantity of electricity passed.

The solution was analyzed for nickel and iron at the beginning and end of each run, and the nickel and iron content of the portion of the sludge soluble in dilute hydrochloric acid was determined. In this way no error was introduced by the presence in the sludge of particles of metallic nickel or nickel oxide, which might have become detached from the anode but which are insoluble in dilute hydrochloric acid. The increase in weight of the cathode represented the weight of the deposited nickel and iron. As the electrochemical equivalents of nickel and ferrous iron are very close, no appreciable error was involved in considering the weight of the small amount of iron usually present as equivalent to nickel.

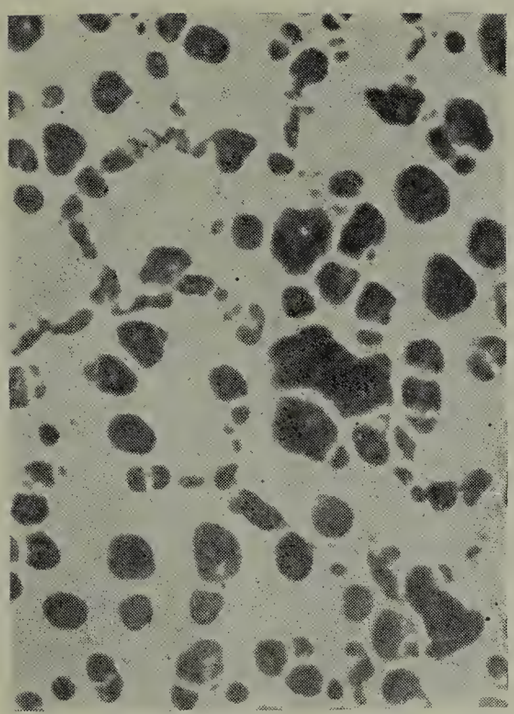
If we let

A = Increase in weight of cathode,
B = Increase in total content of nickel plus iron in the 600 cc. of solution. (If there is a decrease in nickel content, B is negative),
C = Weight of nickel plus iron in the soluble sludge,
D = Weight of nickel equivalent to the weight of copper deposited in the coulometer,
E = Percentage anode efficiency,

then

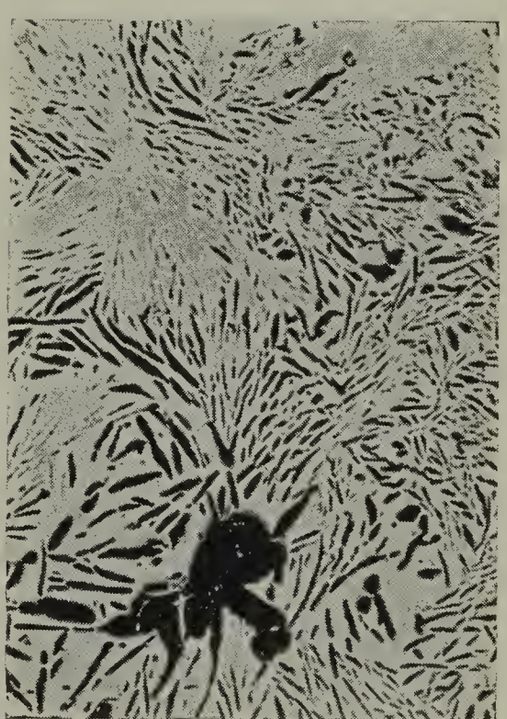
$$E = 100 \frac{A + B + C}{D}$$

Preliminary experiments indicated that, as might be predicted, the anode efficiency is increased by an increase in acidity (decrease in pH). As, however, good deposits can be secured only



A

B



C

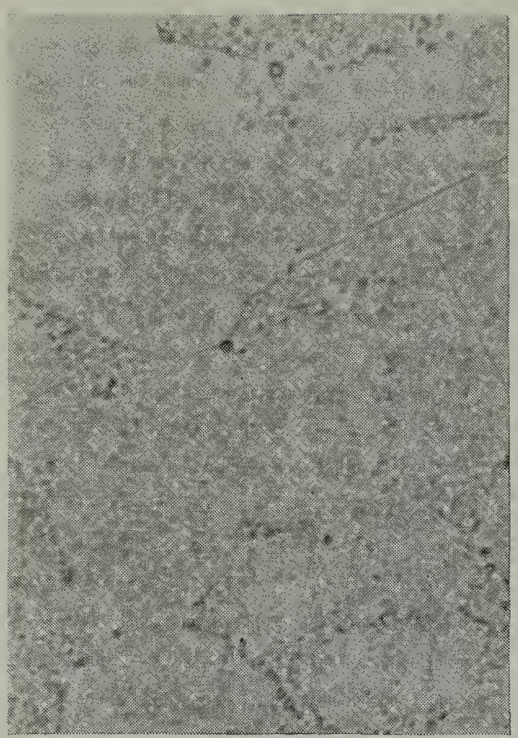
A.—Globular, Anode No. 8

B.—Intermediate, Anode No. 11

C.—Flaky, Anode No. 14

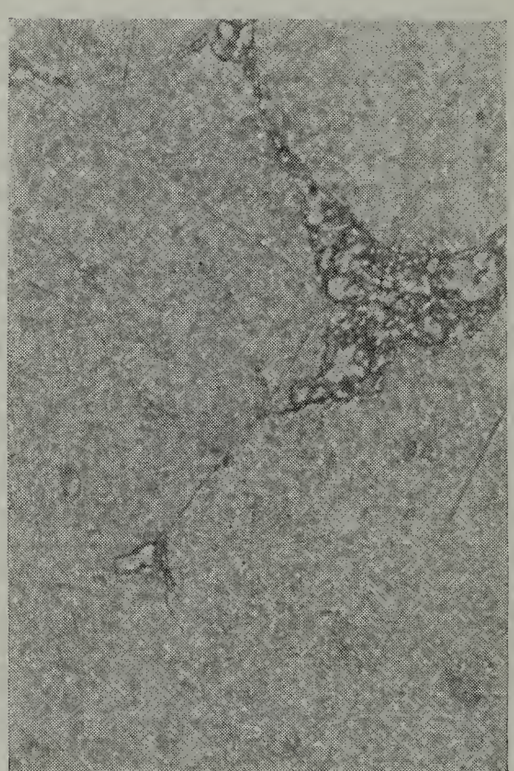
All unetched. All x 50

FIG. 1. FORMS IN WHICH CARBON OCCURS IN CAST ANODES.



A

B



C

A.—Nickel-Nickel Oxide Eutectic, Anode No. 3. The oxide forms with the nickel a eutectic along the grain boundaries.

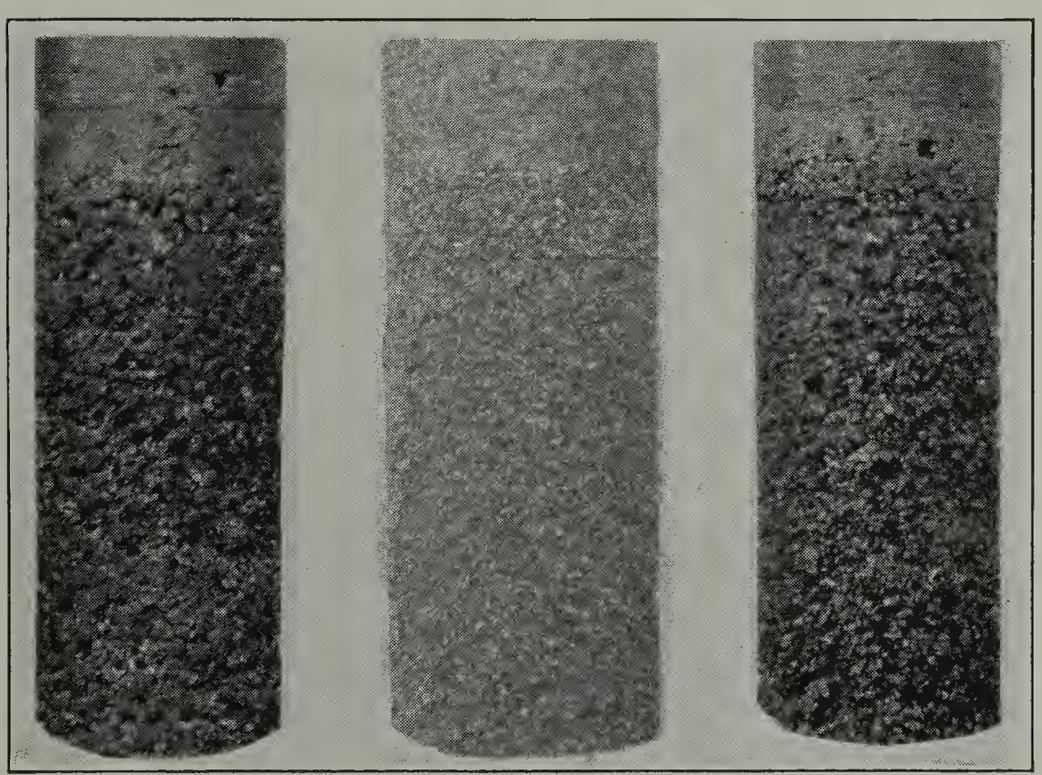
B.—Nickel Sulfide, Anode No. 9. The nickel sulfide inclusions occur both along the grain boundaries and within the grains.

C.—Nickel-Magnesium, Anode No. 10. If magnesium is added in excess of the amount needed to combine with sulfur present, Ni_2Mg is formed along the boundaries.

All x 500.

FIG. 2. INCLUSIONS WHICH AFFECT THE CORROSION OF CAST ANODES.

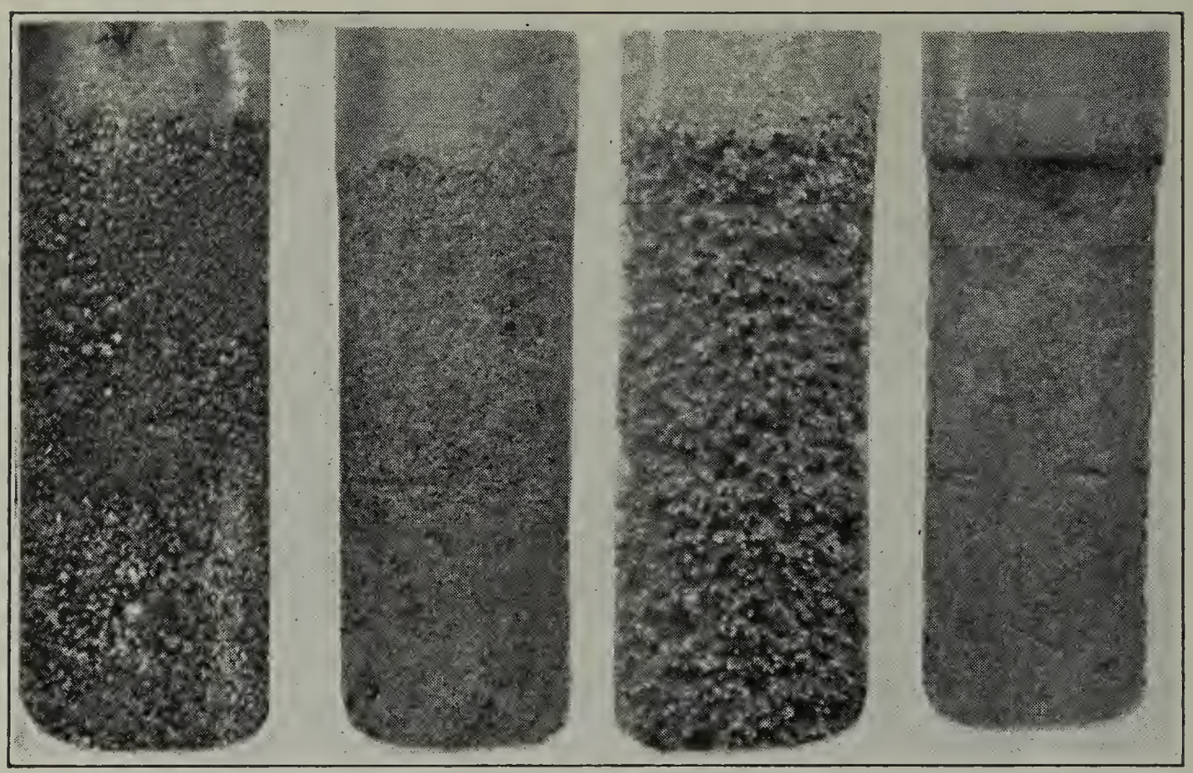
1 2 3



4 5 6

FIG. 4. APPEARANCE OF ANODES AFTER CORROSION.

1. Electrolytic
2. Hot rolled
3. Sand cast, 0.5 per cent NiO
4. Sand cast, 0.1 per cent C
5. Chilled cast, 0.5 per cent C
6. Sand cast, 0.5 per cent C

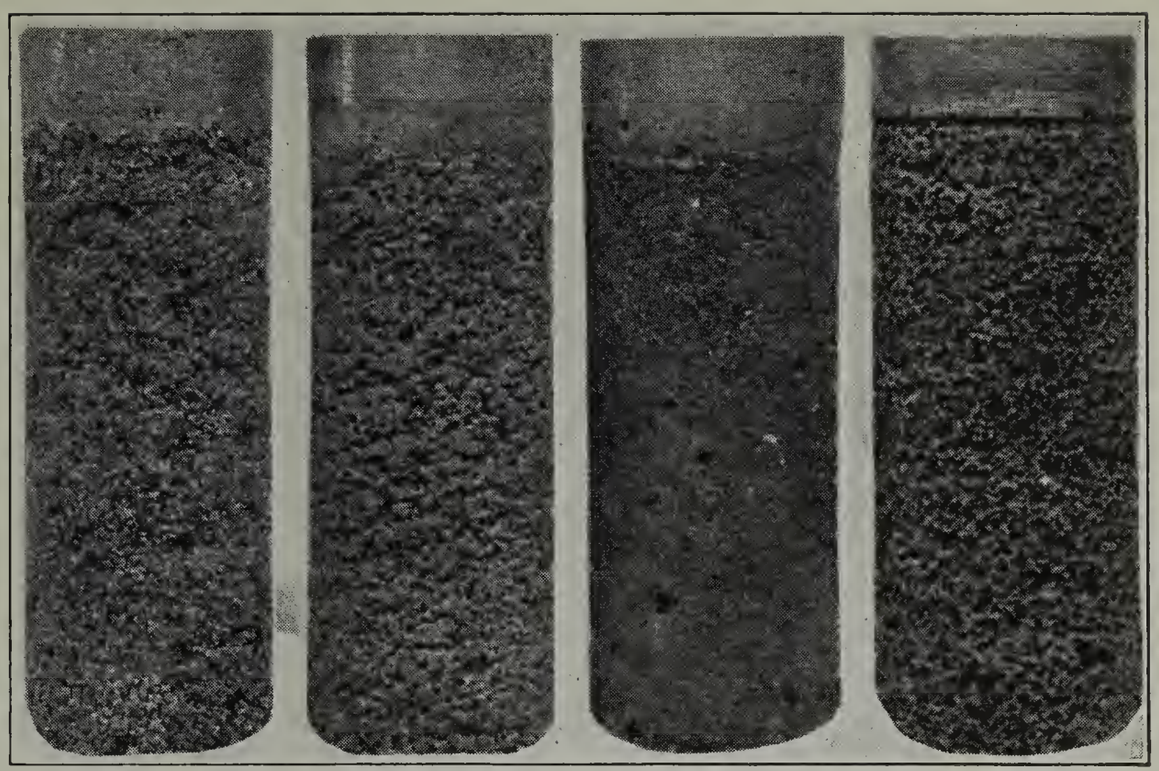


7 8 13 14

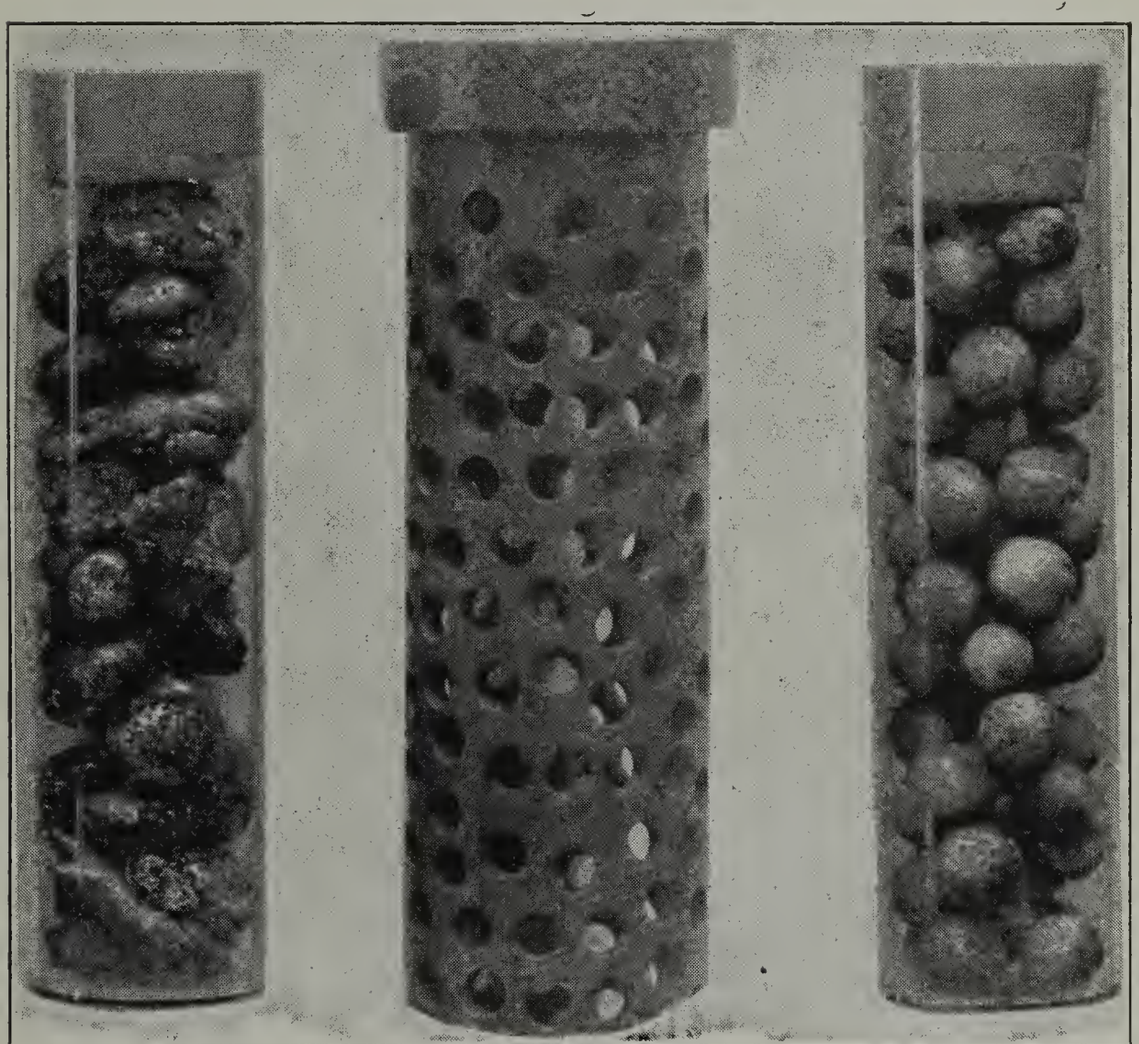
15 16 17 18

FIG. 5. APPEARANCE OF ANODES AFTER CORROSION.

7. Chilled cast, 1.5 per cent C
8. Sand cast, 1.5 per cent C
13. Sand cast, 0.1 per cent C; 1.0 per cent Fe
14. Sand cast, 1.5 per cent C; 1.0 per cent Fe
15. Sand cast, 1.5 per cent C; 5.0 per cent Fe
16. Sand cast, 1.5 per cent C; 1.0 per cent Si
17. Sand cast, 1.5 per cent C; 1.0 per cent Cu
18. Sand cast, 1.5 per cent C; 1.0 per cent Sn



9 10 11 12



19 H 20

FIG. 6. APPEARANCE OF ANODES AFTER CORROSION.

9. Sand cast, 0.5 per cent C; 0.2 per cent S
10. Sand cast, 0.5 per cent C; 0.2 per cent S with Mg
11. Sand cast, 1.5 per cent C; 0.2 per cent S
12. Sand cast, 1.5 per cent C; 0.2 per cent S with Mg
19. "A" shot. 20. Mond shot. H. Shot holder.

from solutions within a rather narrow pH range, about 5.5 to 6.5, results on the anode efficiency in more acid solutions have little practical significance. Therefore in all the experiments the initial pH was adjusted to 5.8, as measured with brom-cresol purple. Only if the anode efficiency was low, say less than 90 per cent, did the pH decrease appreciably. In the latter part of such runs the anode efficiency was probably higher than it would have been with a constant pH. The exact anode efficiency of poorly corroding anodes is however of little practical significance. With anode efficiencies above 90 per cent, the change in pH in a run was not sufficient to affect the results appreciably.

All runs were made at about 25° C. (77° F). At higher temperatures, the anode efficiencies would be somewhat higher. The two current densities employed, *viz.*, 0.5 amp./sq. dm. (4.6 amp./sq. ft.) and 1.5 amp./sq. dm. (14 amp./sq. ft.) were selected to represent respectively the average practice, and an unusually high anode current density for solutions used at ordinary temperature.

Anode Potentials.—The passivity of nickel is made evident when it does not readily assume a true equilibrium potential in its solutions, and does not corrode anodically until the potential is appreciably above (more positive than) the static single potential of nickel. The static potentials are often erratic and difficult to measure.[9] As, however, in electrolysis we are concerned principally with operating potentials, no effort was made to measure the exact equilibrium potentials of the various anodes in the different solutions. Instead, the potentials were measured during electrolysis at several current densities, against a normal calomel electrode, the tip of which was pressed closely against the anode surface. The results recorded are expressed with reference to the normal hydrogen electrode, that is, + 0.283 v. has been added to the calomel electrode values. The potentials are given the sign of the metal with respect to the solution according to the usage adopted by the American Electrochemical Society. The results obtained for appreciable current densities were found to become constant and reproducible in from ten to twenty minutes. In order to have in each case a freshly corroded nickel surface, the anodes were run in a solution containing chlorides for about 0.5 hr. at 1

[9] Schoch, *loc cit.*

amp. / sq. dm. (9.3 amp./sq. ft.), before making any potential measurements. Potential measurements were made upon only a sufficient number of the anodes to represent the various principal types.

TABLE IV.

Nickel Anode Efficiencies.

Solution		1 Chloride		2 Double Salt		3 Single Salt	
Current density, amp./sq. dm.		0.5	1.5	0.5	1.5	0.5	1.5
Current density, amp./sq. ft.		4.6	14	4.6	14	4.6	14
Anode No.	Description	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
1	Electrolytic	100	97	53	19	36	21
2	Rolled	100	97	68	44	68	40
3	Oxidized	100	100	90	86	73	45
4	0.1 C; sand	99	98	80	65	84	70
5	0.4 C; chill	100	97	91	83	91	75
6	0.4 C; sand	99	98	89	86	91	75
7	1.4 C; chill	99	98	93	92	93	93
8	1.4 C; sand	99	97	96	93	95	92
9	0.5 C + 0.15 S	98	97	93	93	95	92
10	0.5 C + Mg	98	97	78	68	77	68
11	1.5 C + 0.15 S	98	98	94	94	95	93
12	1.5 C + Mg	99	97	90	90	92	90
13	0.1 C + 1.5 Fe	98	97	78	60	80	60
14	1.5 C + 1.5 Fe	99	99	96	86	96	95
15	1.0 C + 6.0 Fe	99	95	93	88	93	92
16	1.5 C + 1.6 Si	95	93	94	93	94	94
17	1.5 C + 1.0 Cu	100	98	100	93	95	95
18	1.5 C + 1.0 Sn	99	98	83	80	89	81
19	A Shot	98	98	83	80	89	81
20	M Shot	99	97	80	44	60	38

VI. RESULTS.

The anode efficiencies obtained with the solutions listed in Table III are shown in Table IV, and the single potentials in Table V and Fig. 3.

From Table V it may be noted that the bath potential or overall voltage bears a direct relation to the anode polarization, an increase in which may cause a marked increase in power consumption. An abnormally high bath potential is often an indication of anode passivity. When nickel is passive at a high current

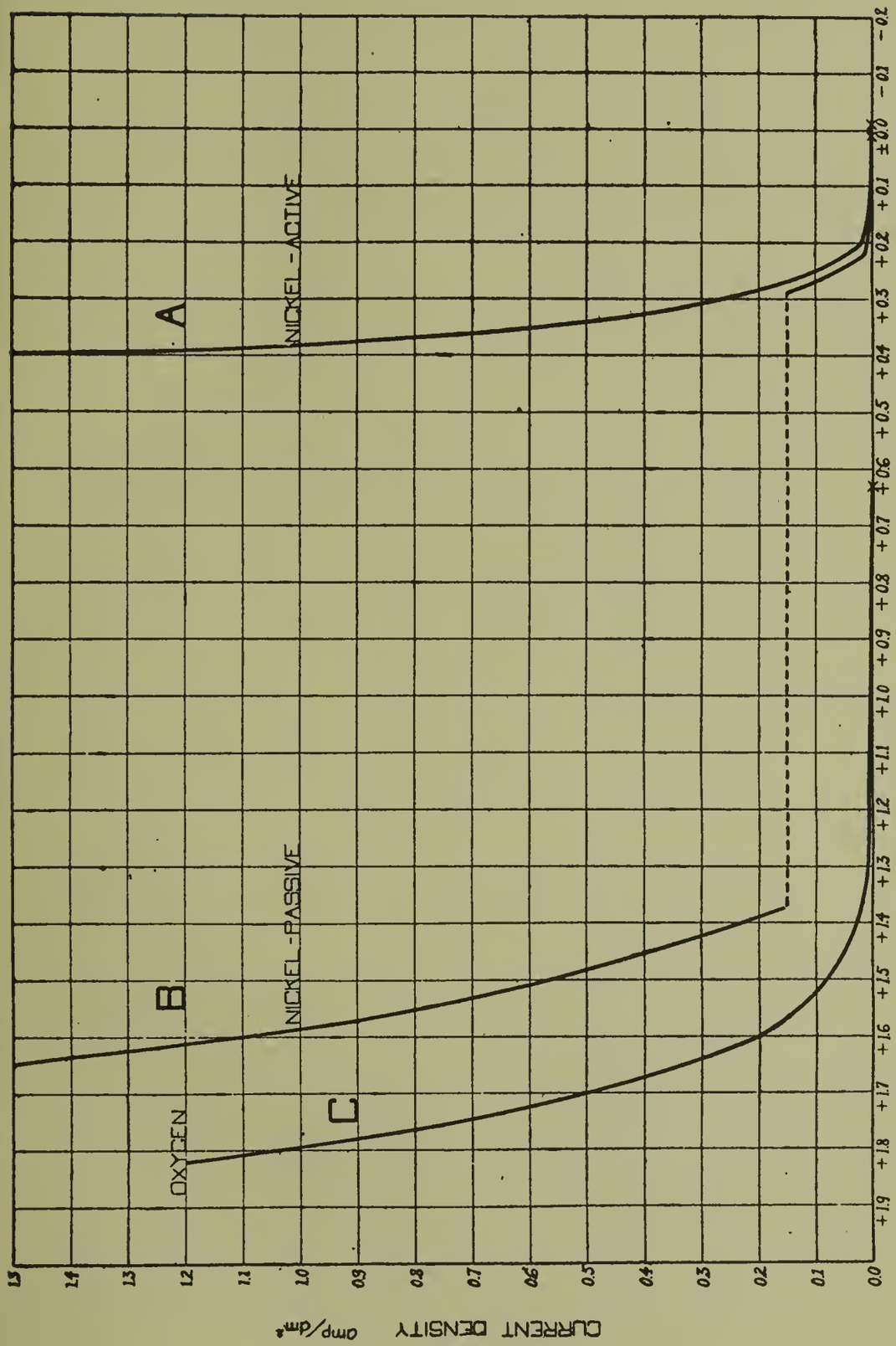


FIG. 3. TYPICAL NICKEL ANODE POTENTIAL-CURRENT DENSITY CURVES

A.—Anodes in solutions containing chlorides.
B.—Anodes in solutions free from chlorides.
C.—Oxygen evolution on nickel anodes.

density, a black deposit of nickelic hydroxide, $Ni(OH)_3$, is likely to form upon the anode.

TABLE V.

Anode Potentials at 21° C. (70° F.)

e_h = Single potential against normal hydrogen electrode, in volts.
V = Over-all or bath potential during operation, in volts.

Solution.....			1 Chloride		2 Double Salt		1 Single Salt	
Anode No.	Description	c.d. amp/ sq. dm.	e_h	V	e_h	V	e_h	V
1	Electrolytic...	..	—0.12	...	—0.01	...	—0.03	...
		0.1	+0.36	0.90	+0.37	0.95	+0.33	0.95
		0.5	+0.46	1.20	+1.66	2.45	+1.66	2.50
		1.5	+0.50	1.55	+1.86	2.95	+1.78	3.20
2	Rolled.....	..	+0.20	...	+0.08	...	+0.02	...
		0.1	+0.39	0.95	+1.44	2.10	+1.50	2.10
		0.5	+0.46	1.25	+1.55	2.40	+1.62	2.55
		1.5	+0.48	1.60	+1.68	2.95	+1.71	3.20
3	Oxidized.....	..	—0.06	...	+0.02	...	+0.04	...
		0.1	+0.05	0.65	+0.12	0.75	+0.16	0.70
		0.5	+0.12	0.90	+1.48	2.35	+1.55	2.50
		1.5	+0.17	1.30	+1.61	2.90	+1.70	3.45
5	0.4 C; chill...	..	+0.19	...	+0.24	...	+0.16	...
		0.1	+0.38	0.90	+1.39	2.00	+1.33	1.95
		0.5	+0.41	1.20	+1.50	2.35	+1.48	2.40
		1.5	+0.48	1.55	+1.64	2.80	+1.62	3.00
6	0.4 C; sand...	..	+0.17	...	+0.20	...	+0.20	...
		0.1	+0.34	0.90	+0.42	1.05	+1.20	1.70
		0.5	+0.44	1.25	+1.53	2.35	+1.44	2.35
		1.5	+0.53	1.65	+1.68	2.95	+1.61	3.00
8	1.4 C; sand...	..	—0.02	...	—0.03	...	—0.30	...
		0.1	+0.30	0.95	+0.34	1.00	—0.12	0.80
		0.5	+0.39	1.20	+1.40	2.25	+1.33	2.25
		1.5	+0.44	1.65	+1.68	2.70	+1.43	3.00
14	1.5 C + 1.5 Fe.	..	—0.07	...	—0.06	...	—0.08	...
		0.1	+0.14	0.80	+0.12	0.75	+0.08	0.80
		0.5	+0.31	1.20	+1.39	2.10	+1.32	2.25
		1.5	+0.44	1.60	+1.45	2.85	+1.41	3.00

The anode current density-potential curves fall into two principal groups, which represent the sharp distinction in the behavior of nickel in the active and passive conditions. These two types of

anodic behavior are illustrated by curves A and B in Fig. 3, each of which is typical of several curves lying close together and corresponding to slight differences in anode behavior. Curve A represents the behavior of all the anodes in solutions containing chlorides, and B their behavior in solutions free from chlorides. Curve C represents the potential of oxygen evolution. Its exact position is dependent upon the oxygen overvoltage, which is influenced by the physical condition of the anode surface.

It is evident that under the conditions represented by A, the anode efficiency will approach 100 per cent, as the potentials are all less positive than that required for oxygen evolution. On curve B, however, the potentials for all appreciable current densities (*e. g.,* above 0.2 amp./sq. dm. or 2 amp./sq. ft.) are beyond the potential for oxygen evolution. Under such conditions the nickel anode behaves like an oxygen electrode. For any given anode potential and corresponding total current density, the nickel anode efficiency may be calculated from the values (Curve B) of the ordinates corresponding to that potential, and to the current density of oxygen evolution (Curve C) at that same potential. Actually in this figure the oxygen curve has been computed from the observed potentials and nickel efficiencies. In general if such curves have been prepared the anode efficiencies may be predicted from the potentials.

Consideration of the data in Table V shows why it is not possible to measure correctly the relative anode efficiencies of two or more anodes, by immersing them in parallel in the same vessel of electrolyte. Suppose that equally sized pieces of electrolytic nickel (No. 1) and of an oxidized cast nickel (No. 3) were hung as anodes on the same rod in a plating bath containing chlorides. Under these conditions it would be observed that No. 3 would corrode more rapidly and it might be incorrectly assumed that the electrolytic nickel would not corrode, at least with a high anode efficiency, in such a bath.

Actually, the experiment simply shows that the cast nickel will corrode, for a given current density, at a lower (less positive) single potential than will the electrolytic nickel, and that in consequence, a larger proportion of the current will go to the cast than to the electrolytic nickel. As a result of the higher current density

thus produced on the cast anode, more metal will dissolve from it in the same time than from the electrolytic, in spite of the fact that the percentage anode efficiency with both anodes may be nearly 100 per cent when the appropriate potentials are applied to each separately. The same relations will apply if instead of having the two kinds of anodes in the same bath, they are placed in separate but similar baths in parallel, and the same potential is applied to each bath.

If, as is the case in a solution containing chlorides, the difference in the potentials required for a given current density is only a few tenths of a volt, it has almost no economic significance in electroplating. If, however, the difference in potential is over one volt (as between the anodes in bath No. 1 and in baths containing no chloride) the power loss due to the passivity of the anodes may become appreciable. When such a great difference exists in the anode potentials, the more passive anode usually has a low efficiency, that is, oxygen is evolved upon it.

The appearance of the anodes after corrosion is shown in Fig. 4 to 6.

VII. DISCUSSION OF RESULTS.

Composition of Solution.

The most striking feature of Table III is the fact that in solutions containing a chloride (0.25 *N*) the anode efficiency at current densities up to 1.5 amp./sq. dm. (14 amp./sq. ft.) is invariably above 95 per cent, and usually approaches 100 per cent. It has long been known that the presence of chlorides in a nickel solution decreases the passivity, but it is somewhat surprising to find that in such solutions all kinds of anodes will corrode with so nearly perfect efficiency

That the high anode efficiency is due to the absence of passivity is indicated by the fact (Table V) that in no case does the anode show in solutions with chlorides a potential more positive than + 0.53 v, while in the other baths potentials as high as + 1.8 v. were observed.

That the action of the chloride ions is specific, was shown by a few experiments not recorded here, in which sodium fluoride was substituted for the ammonium chloride, in which case the anode

efficiencies were in all cases lower than with the chloride bath, and similar to those in the other two baths. The fact that in fluoride solutions almost no basic sludge is formed, has led many, including one of the present authors, to assume that the anode efficiency must be high in such solutions. The fact that solutions containing fluorides can often be operated satisfactorily is due to the fact that in them the cathode efficiency is usually less than in chloride baths, and that in the more acid range they are better buffered than are the chloride baths. In consequence the pH remains nearly constant, even with low anode efficiencies.

The results with the "double" and "single" salt baths are so nearly alike that there is no definite evidence that the presence of ammonium ions, apart from chlorides, is beneficial to anode corrosion.

If therefore, as is now common practice in electroplating, the solutions have an appreciable chloride content, any form of clean nickel anodes will furnish the requisite supply of nickel to the solution. In such solutions, therefore, the choice of anodes must depend upon other factors, principally the purity, which may affect the frequency with which they must be cleaned, and the character of the corrosion during electrolysis.

Composition of Anodes.

In view of the uniformly high anode efficiencies in chloride baths, the relative effects upon efficiency produced by constituents added to the nickel must be determined from the results in the other baths, in which there is a considerable variation.

Carbon. The most common addition to nickel anodes is carbon, which is frequently added intentionally to cast anodes in amounts up to 2 per cent. The addition of carbon to nickel lowers the melting point from 1452° C. (2646° F.), the melting point of pure nickel, to 1311° C. (2392° F.), the melting point of the eutectic, which contains 2.2 per cent C. At higher temperatures, amounts of carbon up to 6.4 per cent may be dissolved in the nickel, and on cooling the excess carbon crystallizes out as graphite (Fig. 1), in a form depending in part upon the conditions of casting and cooling. At the eutectic temperature, the maximum content of dissolved carbon is 0.5 per cent. An appreciable amount of

free carbon was always observed in the cast nickel anodes containing over 0.3 per cent of carbon.

The effect of the carbon content in decreasing the passivity and increasing the anode efficiency, may be seen in the results for anodes 4 to 8. This effect is observed when the nickel contains about 0.4 per cent carbon. With about 1.4 per cent carbon, the anode efficiency in the single and double salt baths becomes nearly equal to that in the chloride bath.

The effect of a separate phase present in the nickel will depend upon its electrolytic potential and its distribution. If it is more noble than the nickel, that is, has a lower solution pressure, it will foster electrolytic solution of the nickel. If it is less noble it will tend to dissolve more readily than the nickel. In the latter case if the new phase is segregated along the grain boundaries, it will dissolve and cause the crystals of nickel to be detached and to drop out.

The simplest explanation of the effect of carbon is that the presence of the second phase (graphite) causes the formation of a large number of local couples, in which the single potential of the nickel is more negative (less noble) than that of the graphite, and consequently solution of the former is favored. That the effect of carbon upon the anode efficiency is due principally to the presence of the graphite particles, and not to their shape or distribution, is evident from the fact that only slight differences in potential or efficiency are observed between anodes cast under different conditions.

Any preferences as to carbon content and treatment must therefore rest principally upon the corrosion of the anodes, which is illustrated in Fig. 4 to 6. From these it may be seen that a high carbon content is especially favorable in producing uniform corrosion, owing no doubt to the fact that the large number of graphite particles hinders selective corrosion of the nickel crystals.

In general, high carbon anodes have a "skin" which corrodes less readily than the interior. This behavior is due principally to the fact that in the skin the carbon content is lower, owing to decarburization on the surface during the casting. In order to eliminate the effects of such surface layers, all of the anodes were corroded in a chloride solution for a considerable period before they were subjected to quantitative tests.

Oxide. That the presence of a separate phase affects the anode efficiency is shown by the results for anode 3, consisting of nickel which was melted without deoxidation. This metal contains not more than 0.01 per cent C and is slightly oxidized. From the amount of the nickel-nickel oxide eutectic present as shown in Fig. 2A (about 25 per cent) it is probable that the sample contains about 0.5 per cent NiO, which is less soluble than the nickel. This anode shows a lower polarization, a higher anode efficiency, and corrodes more smoothly than any of the low carbon anodes. There is a slight tendency for particles of the metal to be detached from the anode, and the corroded surface is not so smooth as that of a high carbon anode.

Sulfide. Among the other constituents which form separate phases, is nickel sulfide (Fig. 2B). Experiments with amounts of sulfur less than 0.05 per cent indicate that no appreciable effect is produced upon the behavior of the anode. If, however, 0.15 per cent or more of sulfur is present, there is a marked tendency for irregular corrosion and detachment of particles. This effect is much more pronounced in anodes with low than with high carbon content. The nickel sulfide inclusions are principally along the grain boundaries. The unfavorable effect of nickel sulfide is probably due to the fact that, unlike nickel oxide, it is more soluble than the nickel. In consequence it is dissolved out from the grain boundaries by selective corrosion and causes particles of nickel to be detached.

Magnesium. For the purpose of making nickel malleable, magnesium is frequently added. Its effect is probably due to the combination of the magnesium with the oxygen and sulfur to form magnesium oxide and sulfide. A few efforts to overcome the deleterious effect of sulfur in the cast anodes by the addition of magnesium (anodes 10 and 12) were unsuccessful, as the uniformity of corrosion was not improved by the magnesium addition. Micro-examinatioin of the anodes containing sulfur and magnesium showed the presence in them of magnesium sulfide and magnesium-nickel inclusions (Fig. 2C). As both of these are more readily soluble than nickel, it is natural that they should promote selective and irregular corrosion.

Iron. Iron is present in at least small amounts (up to 0.5 per cent) in almost all cast nickel anodes, and is frequently added intentionally for the purpose of lowering the melting point and increasing the anode corrosion. The results with anodes 13, 14 and 15, show that the presence of iron does not materially improve the behavior of the anode. From the fact that iron forms solid solutions with the nickel we would not expect any marked effect. Thus No. 13, with a low carbon content and 1.45 per cent iron, corroded even less uniformly than No. 4 with low carbon content and no iron. Anodes No. 14 and 15, which contain iron and are high in carbon, were similar to No. 8, with no iron, although the corroded surfaces of the anodes containing iron were slightly smoother.

The anode behavior of itself furnishes no justification for adding iron to nickel anodes. Amounts up to 0.5 per cent, such as may enter accidentally, are probably not deleterious to the deposits[10] although no definite advantages for the presence of iron in electroplating baths has thus far been shown except in special cases. Anodes containing appreciable amounts of iron become coated with a basic sludge, and consequently corrode with a low efficiency and a high polarization unless they are frequently cleaned.

Copper. Copper is never added intentionally to nickel anodes, but is frequently present as an impurity in commercial forms of nickel from which anodes are made. It has been definitely shown[11] that very small amounts of copper in a nickel bath may be very detrimental. It might therefore appear desirable to exclude copper entirely from nickel anodes. Actually, however, it has been found that if only small amounts of copper (*e. g.,* up to 0.3 per cent) are present in the anodes, very little of it passes into solution if the nickel anodes are corroding at a low potential. This is because the true solution pressure of nickel is appreciably greater than that of copper. If, however, the anodes become passive, or if larger amounts of copper (as much as 1.0 per cent, as in anode No. 17) are present, a large part of the copper passes into the solution and causes the formation of dark deposits or even of black nodules on the cathode deposit, especially near

[10] M. R. Thompson, Trans. Am. Electrochem. Soc., 44, 359 (1923).
[11] M. R. Thompson and C. T. Thomas, Trans. Am. Electrochem. Soc., 42, 79 (1922).

the lower edge. No marked beneficial effect of the copper upon the anode efficiency or behavior was observed. It therefore appears desirable to have the copper content as low as possible, preferably not above 0.25 per cent Cu.

Tin. Tin is sometimes added to nickel anodes, either as such or as phosphor-tin. Its chief function is to reduce the melting point, but when added as phosphor-tin it no doubt also serves as a deoxidizer. The tin probably forms a solid solution with the nickel. It has little effect upon either the anode efficiency or the behavior of anodes with high carbon content. The presence of tin in the solution is apparently not detrimental, but it increases the sludge formation upon the anodes or in the solution, through the precipitation of basic tin sulfates. No tin could be detected in the deposited nickel. There appears to be no advantage or justification for adding tin to the nickel anodes unless it can be shown to be of marked value in their casting.

Silicon. A small amount of silicon, derived from furnace linings and slags, is present in all cast nickel. It is also often added as such or as ferro-silicon to nickel anodes for the purpose of improving the casting. In the presence of 1.5 per cent carbon it apparently has little effect upon the anode efficiency or behavior. Its addition must therefore be justified by metallurgical considerations.

Type of Anodes.

It is not possible to consider the type of anode apart from its composition, as the anodes of different types usually have characteristic differences in composition. Of low carbon, pure nickel, there are four distinct types, electrolytic, cast, rolled, and "carbonyl" nickel. All of these show relatively low anode efficiencies in solutions which do not contain chlorides, but all have high efficiencies in solutions containing appreciable chloride. Differences are due principally to their internal structure and consequent tendency for detachment of particles.

Electrolytic nickel usually has a laminated structure, probably caused by interruptions of the current during the refining process. In consequence there is a tendency for thin layers, of almost lacy proportions, to separate, especially if the solution is agitated.

A somewhat similar tendency is observed in the use of the

spherical shot produced by the Mond carbonyl process. Such shot consist of concentric layers caused by successive deposits of nickel. These layers also tend to flake off after part of the sphere has been corroded, especially in agitated solutions.

As previously indicated, cast nickel containing small amounts of oxide appears to corrode better than that with a low carbon content. With anodes of higher carbon content slight differences could be observed between anodes that were chill cast and sand cast. In general the latter corrode more uniformly, owing probably to the greater tendency of the graphite to form fine flakes (Fig. 1C) in the sand castings, instead of globules (Fig. 1A) which were always present in the chill castings, and only occasionally in the sand castings.

The poured shot (No. 19) may be considered as chill cast, low carbon nickel. The corrosion efficiency is similar to that of other low carbon cast nickel. Owing, however, to the fact that the "skin" on the globules is more passive than the interior, and that many of the shot are hollow, there is a tendency for the interior to corrode most rapidly when the shell is penetrated in a few places (Fig. 6). In consequence, fine flakes of nickel may become suspended in the solutions, or choke up the openings in the container for the shot.

The efficiency of rolled anodes in solutions free from chlorides is lower than that of high carbon cast anodes. This fact no doubt underlies the frequent recommendation in European practice, to replace part of the cast nickel anodes with rolled anodes if the solution tends to become alkaline (an evidence of excessive anode efficiency). In solutions containing chlorides, however, the rolled anodes corrode with high efficiencies, and at about the same potentials as do the cast nickel anodes.

The fact that in solutions free from chlorides, rolled nickel and low-carbon cast nickel corrode more readily and with a higher efficiency than does electrolytic nickel, may be due to the presence of strains in the rolled and cast metal, and the fact that strains in metal increase the solution pressure.[12] The higher rate of corrosion of the rolled and cast nickel is apparently more than can be accounted for by differences in composition, especially as the car-

[12] A. J. Allmand, Principles of Applied Electrochemistry, Longmans & Co., p. 135 (1912).

bon in them is completely in solution and so does not have the effect of a separate phase. It is well known that in rolled and cast metal, there is a greater tendency for the existence of strains than in electrolytic metal, which is more nearly in an equilibrium condition.

VIII. SUMMARY.

1. In solutions containing only nickel sulfate and boric acid the anode current efficiency of all forms of nearly pure nickel is low.

2. All forms of clean nickel anodes corrode with high anode efficiency in solutions containing appreciable amounts of chlorides, *e. g.* 0.25 *N* NH_4Cl.

3. The presence of ammonium sulfate or of fluorides in the solutions does not materially increase anode corrosion.

4. The single potentials of anodes during their operation in solutions containing chlorides are less positive than in those without chlorides, which confirms the fact that chlorides decrease the passivity of nickel.

5. Additions of carbon to cast nickel increase anode efficiency and promote uniform corrosion.

6. Carbon-free cast nickel containing nickel oxide corrodes more smoothly, at a less positive potential, and with higher anode efficiency than does low carbon cast nickel.

7. Sulfur is deleterious in cast anodes, as it causes selective corrosion and detachment of particles. This effect is most marked in low carbon anodes and is not overcome by the addition of magnesium.

8. Copper in anodes has little effect on their behavior, but if present in appreciable amounts it will enter the solution and cause inferior cathode deposits.

9. Iron in nickel anodes has a slightly beneficial action upon the smoothness of corrosion, but not sufficient to warrant its intentional addition.

10. Tin and silicon have little effect on the behavior of the anodes. They pass into the sludge and do not directly affect the deposits.

11. Electrolytic and shot nickel anodes show more tendency for detachment of nickel particles than do high carbon cast nickel anodes.

12. As a basis of specification for cast nickel anodes, it is tentatively suggested that they should be sand cast and contain not less than 95 per cent nickel (plus cobalt) and 1.25 per cent carbon, and not more than 0.25 per cent copper or 0.10 per cent sulfur. Iron, silicon and tin may be permitted in amounts up to 1 per cent of each, but are not recommended.

In conclusion the authors desire to express their appreciation for advice and assistance from H. Scott, R. G. Waltenberg and E. Ruh in the preparation of the anodes; to J. A. Scherrer and H. A. Bright in the anode analyses; to J. H. Winkler in the study of the micro-structure, and to H. E. Haring in measuring the electrolytic potentials; also to the International Nickel Co. for furnishing most of the nickel used in the investigation; and to the Research Committee of the American Electroplaters' Society for helpful advice and suggestions.

DISCUSSION.

G. B. HOGABOOM[13]: This paper is of great importance and gives the first published data of any value on electroplaters' nickel anodes. It is to be regretted, however, that the experiments were not continued throughout the life of the different anodes. The time of 120 hr. is too short to obtain commercial conditions. All the data are based upon "clean" anodes, and in practice is it not possible to maintain clean nickel anodes, except when rolled nickel anodes are used. There is an accumulation of sludge in a short time on the cast anodes now used, which has a decided effect on the measurement of potentials. This sludge (showing sample) contains a high percentage of nickel, *e. g.*, on a 95 to 97 per cent nickel anode an average of 84 per cent of metal was found by analysis. But there is little sludge formation on a rolled nickel anode of 99+ per cent nickel; the highest percentage of metallic nickel found was 34.89 per cent. I am led to believe that in anode corrosion the nickel oxide or a chloride is formed first and then the sulfate of nickel.

[13] Research Plater, P. and F. Corbin, New Britain, Conn.

The use of shot nickel as anode in an electroplating bath cannot be recommended. The shot breaks down and forms a fine dust, which destroys the electrical contact between the shot particles, insulating one from another. The dust also clogs the perforations of the container. It is then impossible to obtain accurate potential readings, or to collect any reliable data as to efficiency.

If carbon is present in the anode in the free state (graphitic carbon) it will, upon being released during electrolytic corrosion, float away from the anode and be co-deposited with the nickel, thus destroying the character of the deposit—a very detrimental factor in electroplating. Carbon will also cling to the anode, forming a partially insulating coating, and decrease the anode efficiency. A nickel anode should be as free from graphitic carbon as possible.

The presence of sulfur in a nickel anode is detrimental. To obtain sulfur-free nickel anodes it will be necessary to change most of the present methods of making them. The general practice at present is to melt the nickel in a down-draft fuel oil heated furnace and to mix the shot, or ingot nickel, with anthracite coal. Coal and fuel oil often contain high percentages of sulfur. The rolled nickel anode has many advantages over any other type of anode for electroplating. There is much less sludge formation, and the surface of the anode can be kept fairly clean, if a small addition of chloride is used in the solution. The maintenance of the nickel content of the plating bath through anode corrosion is more constant, and therefore less nickel salts will have to be added. From a comparison of two plating solutions operated for a long time, one with cast anodes and the other with rolled anodes, the metal supplied by the anodes was 60 per cent for the former and 73 per cent. for the latter. In these same solutions there was a decided contrast in the accumulation of sludge in the bottom of the tank. The tank containing the rolled anodes had less than 25 per cent as much sludge as the tank in which cast anodes were used. The nickel metal content of the sludge was over 80 per cent for the cast anodes and practically zero for the rolled anodes.

Messrs. Thomas and Blum's paper indeed emphasizes the necessity for closer co-operation of the plant with the laboratory, and for more extensive research work in plant operation.

C. P. MADSEN[14]: Many valuable data are given on the performance of commercially available anodes, but the small scale of the tests has not given the authors a realization of the relative order of importance of nickel anode defects in commercial scale operation.

My own anode research was carried out on a scale of opposite extreme in size, in which perhaps some troubles were exaggerated as compared with what they would be in ordinary electroplating. One cell contained ten tons of anodes, divided into twenty castings weighing a thousand pounds each, and was operated continuously for thirty days at 36 amp. per sq. ft. of cathode surface. The cathode was a rotating cylinder, and when the deposit was removed and spread out, it measured 5 by 24 feet (1.5 x 7.3 m.). Several were over 0.125 in. (3 mm.) thick. In this case the sludge problem, which Mr. Hogaboom has mentioned, was a very serious matter. The conclusion of the authors that nothing is gained by adding iron, tin, and silicon was not only confirmed in these experiments, but the general conclusion was reached that absolutely nothing can be added to a nickel anode which will not afterwards cause trouble. Furthermore, the effect of very small amounts of other elements already in the nickel from which the anodes are made is surprising. Traces of chromium and of oxygen are the most serious in the effect upon the solubility of the anode, but traces of other elements, as for instance lead and iron, injuriously affect the structure of the cathode metal deposited.

The result of this work was the development of the final anode described in my paper[15] on "Mechanically Perfect Electrolytic Nickel," which anode seems to afford a solution, for the present, of the nickel anode problem. One difficulty with this anode of mine, however, is that at the present time it cannot be made economically less than two inches thick. It is to be regretted that this anode was not known to Messrs. Thomas and Blum at the time their tests were carried out.

S. SKOWRONSKI[16]: May I ask how the metal is deoxidized in an electric furnace?

[14] Consulting Engr., New York City.
[15] This volume, page 249.
[16] Research Chem., Raritan Copper Wks., Perth Amboy, N. J.

C. P. MADSEN: The metal is deoxidized in the ladle. It is all ladle casting, and part of the procedure is still a secret. The main point is to avoid manganese and add magnesium instead. Use first green poles and then magnesium and do it extremely fast. The whole operation has to be carried out in a few seconds.

S. SKOWRONSKI: Some years ago in the electro-refining of nickel, we added manganese dioxide to the nickel anodes, and while only a trace was added, the manganese built up in the electrolyte until finally it deposited along with the nickel upon the cathode, forming sharp needles which caused short circuits.

FLOYD T. TAYLOR[17]: It has always seemed to me that in a cast anode we ought to have a binder that will hold the particles of nickel in mechanical suspension and in semi, if not in perfect, electrical contact until all the nickel is absorbed by the solution. Without such a binder, nickel particles may become detached from the anode, slide off into the bottom of the tank, out of the path of the current, and be lost as far as contributing to the metal content of the solution is concerned.

The paper just presented is interesting in one or two other points. For example, it clearly indicates that there is no inherent value in the physical section of the anode; that is, the rate of dissolution of an anode is not a function of its cross section. The paper shows that the modern trend towards the purer cast anode is a trend in the right direction. Years ago the two ordinary commercial anodes were the 85/87 per cent nickel and the 90/92 per cent nickel anode. It was often stated that it was necessary to add iron to make nickel anodes dissolve properly. Later the 95/97 per cent cast nickel anode was developed. It did dissolve properly and nicely, and was certainly a step in the right direction.

The statements which have been made regarding shot nickel are interesting, because shot nickel possesses some features which are commercially attractive, yet I agree with Mr. Hogaboom that we have not yet solved some of the difficulties presented by the use of shot nickel, and these difficulties will have to be removed if the use of shot nickel is to be practical.

Rolled nickel anodes, as you know, have been very popular in England. We believe, however, that the wide adoption of rolled

[17] Vice-Pres., A. P. Munning and Co., Matawan, N. J.

nickel anodes in America would mean that our platers would have to become used to the control of nickel solutions with rolled nickel anodes, as against the present almost universal policy of using high-grade cast nickel anodes. At this time, and certainly in the recent past, the use of rolled nickel anodes would be more expensive than the use of the cast nickel anode. Such research work as this well illustrates the great value of this Society to the practical plater.

COLIN G. FINK[18]: Mr. Hogaboom, how much sulfur is in that sludge you are showing us?

G. B. HOGABOOM: Our analyst reported copper 0.91 per cent, iron 4.10, and insoluble 7.21 per cent.

EDWIN SMITH, JR.[19]: In this discussion anodes are spoken of as containing 97 per cent of nickel. At the Edison Storage Battery Co. we are plating large quantities of nickel. The anodes invariably contain 99 per cent. of nickel. We find that there is quite a difference in the way different lots of anodes act, according to their physical structure. We are just going into that at the present time. We limit the copper to 0.4 per cent and the iron to 0.4 per cent. The carbon usually runs 0.1 per cent and the sulfur 0.1 per cent, while the iron and the copper together usually are not more than 0.7 per cent. Some lots of anodes give us perfect plating with a current density as high as 150 amp. per sq. ft. (17 amp. per sq. dm.) and other lots do not. The chief difference is found to be in the physical structure of the anode itself rather than in its chemical composition.

G. B. HOGABOOM: Mr. Smith evidently has not appreciated that the anode I mentioned, of which the analysis is 99.75 nickel and 0.25 per cent iron, contained absolutely nothing else.

EDWIN SMITH, JR.: I may add that we have never had an opportunity to get an anode of that high purity.

[18] Head, Division of Electrochemistry, Columbia Univ., New York City.
[19] Chief Chemist, Edison Storage Battery Co., Orange, N. J.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

CONDUCTIVITY OF NICKEL DEPOSITING SOLUTIONS.[1]

By L. D. Hammond.[2]

Abstract.

The conductivity of solutions of nickel sulfate of various concentrations was measured, and the effect upon the conductivity of common additions to nickel plating baths was determined. Ammonium chloride was found to have the greatest relative effect in decreasing the resistivity, and a beneficial action on the formation of good deposits.

For some time the Bureau of Standards has been engaged in a study of nickel deposition. Because good conductivity of electrolytes is useful in reducing power costs, is an important factor in the "throwing power" of solutions[3] and influences certain characteristics of deposits, such as smoothness, a study was made of the effect of the common additions to nickel baths upon the resistivity of nickel sulfate solutions.

In a list of formulas of such solutions collected by O. P. Watts[4] it is shown that many compounds, both organic and inorganic, have in the past been used or proposed. With the scientific control of nickel plating solutions has come a tendency toward simpler composition. Organic compounds are now seldom used. Inorganic substances may be added to increase the conductivity, to regulate the acidity, to reduce the metal ion concentration or to aid anode corrosion. Frequently a single substance serves several of these purposes. Only compounds typical of those used commercially were included in this investigation.

[1] Published by permission of the Director, U. S. Bureau of Standards. Manuscript received February 15, 1924.

[2] Bureau of Standards, Washington, D. C.

[3] H. E. Haring and W. Blum, Trans. Am. Electrochem. Soc., **44**, 313 (1923).

[4] Trans. Am. Electrochem. Soc., **23**, 123 (1913).

As the primary object of this study was to obtain information for the benefit of the plating industry, no attempt at precision measurements was made. The data obtained are probably accurate to one per cent or better.

The measurements were made at 25° C. with a Leeds and Northrup slide wire bridge of the Kohlrausch type, and a resistance box with Curtis coils. A cell of the burette form, with platinized platinum electrodes, and with a cell constant of 10.14 ohms, was employed. A. C. current with a frequency of 1,000 cycles was supplied by a constant speed high-frequency generator.

With the exception of nickel sulfate, nickel chloride and sodium fluoride, all the salts used were recrystallized once from solutions of the C. P. grade of material. The sodium fluoride was obtained by filtering a solution of a C. P. salt which was free from chlorides, sulfates and carbonates into a platinum dish, evaporating to dryness and finally drying at 110° C. A determination of the fluoride content of such material by means of the lead chloro-fluoride method yielded results close to the fluorine content calculated for NaF.

The nickel sulfate used was prepared from a salt found to contain only small amounts of copper, cobalt, iron, calcium and magnesium. Barium hydroxide was added to a solution of this material, until an appreciable precipitate of nickel hydroxide was formed. As the hydroxides of copper and iron (and of most of the other heavy metals) are precipitated at a lower pH than is nickel hydroxide (pH = 6.7), such metals were carried down with the nickel hydroxide. The filtered solution was then evaporated and allowed to crystallize. The nickel sulfate thus prepared showed spectroscopic traces of cobalt and barium and about 0.001 per cent of calcium. The nickel chloride was found to contain iron but no calcium. Its solution was treated with chlorine, boiled and then neutralized with nickel hydroxide, filtered and crystallized.

The cell constant was determined with a normal solution of recrystallized potassium chloride, using Kohlrausch's value of 0.1118 reciprocal ohm-cm. as the specific conductivity at 25° C. Quite recently[5] some question has arisen as to the absolute value

[5] Kraus and Parker. J. Am. Chem. Soc., 44, 2425 (1922).

of this figure, but any error in this value is doubtless insignificant in work of the moderate accuracy involved in this paper.

The results of these measurements are reported as resistivity in ohm-centimeters Ω-cm. (ohms per centimeter cube) instead of as

TABLE I.

Resistivities of Solutions at 25° C. (77° F.) in Ohm-Cm.

Name	Formula	Concentration		
		N	0.5 *N*	0.1 *N*
Hydrochloric acid....	HCl	3.07	5.66	26
Sulfuric acid.....	H_2SO_4	4.81	9.29	40
Hydrofluoric acid....	HF	....	81	279
Acetic acid.....	$HC_2H_3O_2$	671	870	1,920
Boric acid.....	H_3BO_3	69,900	21,700	*
Potassium hydroxide.	KOH	5.07	9.48	46
Potassium chloride...	KCl	8.94	17.1	78
Potassium cyanide...	KCN	8.21	15.3	70
Sodium hydroxide....	NaOH	5.77	10.6	50
Sodium chloride.....	NaCl	11.57	21.7	92
Sodium fluoride.....	NaF	18.5	29.4	121
Sodium sulfate.....	Na_2SO_4	16.8	29.1	109
Sodium carbonate....	Na_2CO_3	18.7	31.3	117
Sodium phosphate....	Na_2HPO_4	31.5	52.4	199
Ammonium hydroxide	NH_4OH	971	1,280	2,700
Ammonium chloride.	NH_4Cl	9.04	17.2	78
Ammonium sulfate...	$(NH_4)_2SO_4$	12.9	23.0	94
Calcium chloride.....	$CaCl_2$	13.2	23.8	101
Magnesium sulfate...	$MgSO_4$	29.9	49.5	171
Copper sulfate.....	$CuSO_4$	34.1	56	191
Zinc sulfate.....	$ZnSO_4$	32.1	53	187
Zinc chloride.....	$ZnCl_2$	13.4	22.6	101
Cadmium sulfate.....	$CdSO_4$	38.0	62	210
Cadmium chloride....	$CdCl_2$	40	58	185
Ferrous chloride.....	$FeCl_2$	14.5	25.2	...
Ferrous sulfate.....	$FeSO_4$	31.6	53	181
Ferrous ammonium sulfate	$FeSO_4.(NH_4)_2SO_4$	12.0	....	...
Nickel sulfate.....	$NiSO_4$	34.4	53	195
Nickel ammonium sulfate	$NiSO_4.(NH_4)_2SO_4$	....	19.5	71
Nickel chloride.....	$NiCl_2$	14.1	25.0	105
Cobalt sulfate.....	$CoSO_4$	34.1	57	204
Cobalt chloride.....	$CoCl_2$	14.5	25.3	75
Silver potassium cyanide	$KAg(CN)_2$	....	16.0	...
Lead fluoborate.....	$Pb(BF_4)_2$	9.2	....	...

* Concentrations of boric acid are *M*.

conductivity in reciprocal ohm-centimeters. This has the advantage of expressing a determined value instead of a derived relation. For these solutions the resistivity values are greater than unity, which fact slightly simplifies their comparison.

Most of the measurements of resistivity of solutions recorded in the literature were made at 18° C., the concentrations were expressed in terms other than in the normal system, and the results were expressed as conductivity in reciprocal ohm-centi-

TABLE II.

Comparison of Resistivities of Solutions.

Salt	Conc. *N*	Spec. Cond. 25° C. Recorded Mho-Cm.	Spec. Resist. Calculated Ohm-Cm.	Spec. Cond. 25° This paper Mho-Cm.	Spec. Resist. This paper Ohm-Cm.
$NiSO_4$.....	1	0.02909 *	34.37	0.02906	34.41
$NiSO_4$.....	2	0.0450 †	22.22	0.0450	22.22
$NiSO_4$.....	3	0.0531 †	18.83	0.0526	19.01
$NiSO_4$.....	4	.....	.....	0.0547	18.28
$MgSO_4$.....	1	0.0334 ‡	29.94	0.0334	29.94
K_2SO_4.....	1	0.0822 †	12.17	0.0823	12.15
Na_2SO_4.....	1	0.0594 †	16.84	0.0594	16.84
$(NH_4)_2SO_4$.	1	0.0780 †	12.82	0.0795	12.58
$NiCl_2$.....	1	0.0707 ¶	14.14	0.0702	14.25
NaCl.....	1	0.0864 §	11.57	0.0864	11.57
NH_4Cl.....	1	0.1106 †	9.04	0.1115	8.97

* H. C. Jones. Electrical Conductivity, etc., of Certain Salts and Organic Acids (1912). Calculated to the international reciprocal ohm by using the factor 1.066.

† Kohlrausch and Holborn (1916). Extrapolated from data at 18° C.

‡ Jones and Caldwell, Am. Chem. J., **25**, 371 (1901).

¶ A. Heydweiller, Z. f. anorg. Chem., **116**, 44 (1921). Extrapolated from data at 18° C.

§ Stearns, J. Am. Chem. Soc., **44**, 674 (1922).

meters. Furthermore, some data were expressed in terms of the Siemens reciprocal ohm, the value of which is about 6 per cent larger than the international reciprocal ohm, which is used throughout this paper. For convenience of reference, Table I, with the resistivities of pure solutions of substances commonly used in the plating industry, has been compiled from various sources. Certain values have been computed from data at 18° C., using known or assumed temperature coefficients. The values are probably correct to one per cent.

The probable precision of the results obtained in this research is indicated in Table II, in which the results of the measurements upon solutions of the individual salts are compared with the resistivities computed from the conductivities recorded in the literature, as far as these were found to be available.

In general, the agreement with admittedly more precise measurements is within one per cent. The discrepancies with the ammonium salts are probably due to the fact that these salts were crystallized from a solution saturated at the boiling temperature and may have contained traces of acid, produced by hydrolysis.

TABLE III.

Resistivity of Normal Nickel Sulfate Solutions Containing Added Compounds.

$\cap$ - cm, at 25° C. N - $NiSO_4$ = 34.4 $\cap$ - cm.

Added Compound	Na_2SO_4	K_2SO_4	$(NH_4)_2SO_4$	$MgSO_4$	NaCl	NH_4Cl	$NiCl_2$*	NaF	H_3BO_3†
Conc. N									
0.1	29.4	28.1	28.0	31.5	27.0	26.0	....	28.8	33.9
0.2	26.2	24.2	24.0	29.4	22.5	21.1	27.2	25.5	34.1
0.4	....	....	18.8	....	....	15.3	....	....	....
0.5	20.0	....	....	25.3	15.4	....	20.5	....	35.0
1.0	15.0‡	....	....	21.1	10.5	....	....	....	....

* The total concentration of nickel in these solutions was N; *i. e.*, nickel chloride was substituted for the equivalent of nickel sulfate.

† Molar concentrations.

‡ Interpolated from results at somewhat different concentrations.

A normal solution of the ammonium chloride thus prepared had a pH (to methyl red) of 5.10, while a solution prepared from a small quantity of ammonium chloride purified by sublimation gave a pH of 5.75.

In Table III are listed the resistivities of nickel sulfate solutions containing specified amounts of different inorganic compouds. Normal nickel sulfate solution was used as a basis, because it is typical of the concentration generally employed in the industry. The decrease in resistivity (Table II) of nickel sulfate solutions upon increasing the concentration beyond 2 N is probably not sufficient to warrant the use in electroplating of higher concentrations,

in view of the increased cost for material and the loss of solution involved in handling the plated articles. This becomes an important factor when the installation is large.

The data for nickel solutions containing sodium fluoride, ammonium sulfate, potassium sulfate and ammonium chloride could not be continued much beyond the concentrations indicated on account of the formation of sparingly soluble double salts. The relative

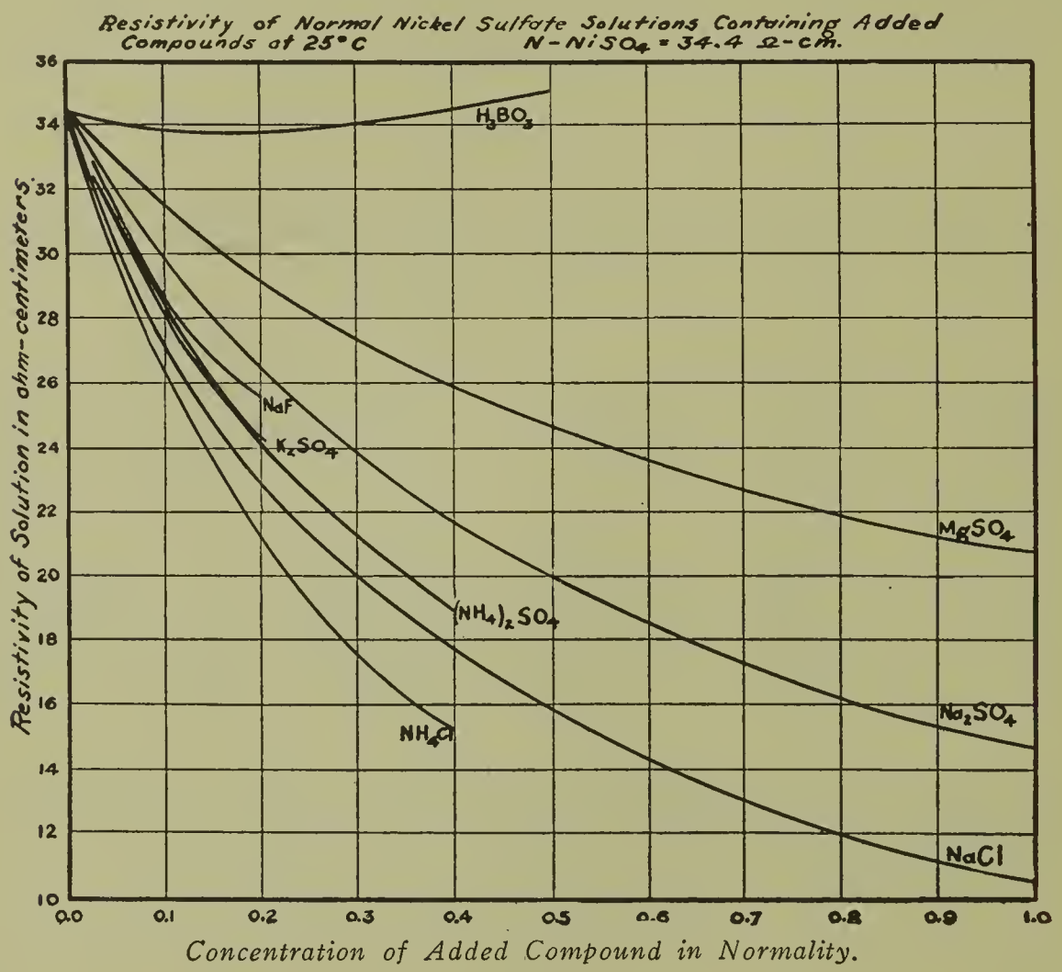


FIG. 1

effects of the various additions are illustrated graphically in Fig. 1. The slight increase in the resisitivity of nickel sulfate caused by 0.5*M* boric acid is practically neglible. Observations on a few solutions containing *N* nickel sulfate, a 0.2 *N* concentration of a salt such as sodium sulfate, ammonium chloride, or sodium fluoride, and 0.5 *M* boric acid, showed that the presence of the latter always slightly increased the resistivity, just as with the nickel sulfate alone.

It has been shown[6] that the addition of magnesium sulfate increases the resistivity of strongly acid zinc sulfate solutions and that the sulfates of iron and nickel[7] have a similar effect on strongly acid copper refining electrolytes. In such solutions the conductivity is due principally to the hydrogen ion content of the acid in the electrolytes, and this is reduced by the common ion effect of the added sulfates. However, *N* nickel sulfate is practically neutral (pH = 6.7) and the addition of the solution of any well ionized neutral salt will decrease its resistivity. Even salts with common ions, such as the sulfates of ammonium, sodium and magnesium, decrease the resistivity, although somewhat less so than those with no common ion, such as the chlorides of ammonium and sodium. The resistivities of nickel sulfate solutions containing added salts were found to be in the same order as, though not directly proportional to, the resistivities of the solutions of the salts themselves. This fact indicates that abnormal effects, such as the formation of complex ions, did not occur to any marked degree.

Of the common additions to nickel solutions, it may be seen that for a given concentration, ammonium chloride produces the greatest improvement in the conductivity. Its general use in nickel solutions probably depends in part upon this property, although it is added primarily to increase the anode corrosion. The choice of the material to add to such solutions to secure the best operating conditions involves numerous considerations of which the conductivity is only one. The generally observed fact, confirmed by us in a few simple experiments, that nickel solutions containing ammonium chloride yield good deposits over a wider range of conditions (such as of pH) than those with other salt additions indicates that this salt is intrinsically beneficial. Such an effect may be due to the fact that in the cathode film, which is usually less acid than the bulk of the solution, there is less tendency to precipitate basic nickel compounds if ammonium salts are present, than if they are absent. Further studies will be required to explain the effects of different constituents upon cathode deposits.

[6] Tartar and Keyes, Jour. Ind. Eng. Chem., 13, 1127 (1921).
[7] Kern. and Chang. Trans. Am. Electrochem. Soc., 41, 181 (1922).

SUMMARY.

1. The effect of separate additions of sodium sulfate, potassium sulfate, magnesium sulfate, ammonium sulfate, sodium chloride, ammonium chloride, sodium fluoride and boric acid on the resistivity of normal nickel sulfate was determined.

2. Ammonium chloride was found to have the greatest relative effect in decreasing the resistivity, and a beneficial action on the formation of good deposits.

Acknowledgments are due to Dr. William Blum, under whose direction this work was done.

DISCUSSION.

C. P. MADSEN[8]: In large scale operation I have never found it of any advantage to use any other chloride in nickel solutions than nickel chloride. The only objection to its use that I know of, that of high cost, is easily obviated by making it one's self. Nickel chloride, satisfactory for plating purposes, can be made by adding to a normal solution of nickel sulfate some calcium chloride and then filtering at a low temperature. The small amount of calcium sulfate which remains in solution under this condition will cause little harm, and will largely disappear in the subsequent purification of the bath for plating.

G. B. HOGABOOM[9]: In this paper and in Thomas and Blum's paper on "Nickel Anodes,"[10] the value of a chloride in nickel plating is clearly shown. The effect of the chloride concentration on the maintenance of the nickel content of a plating solution is marked. It will be found when using ammonium chloride, that, as the chloride concentration goes down the nickel concentration will follow the same direction of the curve. By maintaining the chlorine ion concentration at a definite point, a high and a fairly constant anode corrosion can be obtained.

There is a difference of opinion as to which of the three

[8] Consulting Engr., New York City.
[9] Research Plater, P. and F. Corbin, New Britain, Conn.
[10] This volume, page 193.

chloride salts generally used, viz., sodium, ammonium and nickel, is the best. That is an excellent subject for a research.

COLIN G. FINK[11]: It might interest our nickel men to know that in electrolytic refining of tin we imitated this scheme of adding a little chloride to our tin sulfate-sodium sulfate electrolyte, and we have been able to get a decidedly uniform corrosion of very impure tin anodes.

EDWIN SMITH, JR.[12]: In regard to the addition of chlorides, we habitually use a solution which contains only nickel in the form of sulfate, with the addition of sodium sulfate occasionally for certain purposes. The chloride present in our solution usually runs about a quarter of a gram per liter, and is derived from the tap water. I am at a loss to account for the *few* troubles with passive anodes under these circumstances.

[11] Head, Division of Electrochemistry, Columbia Univ., New York City.
[12] Chief Chemist, Edison Storage Battery Co., Orange, N. J.

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THE RELATION BETWEEN POLARIZATION AND STRUCTURE IN THE ELECTRODEPOSITION OF METALS.[1]

By V. Kohlschutter.[2]

Abstract.

A close relationship is shown to exist between the abnormal cathode potential in nickel deposition and certain physical properties of the deposit. The paper is essentially a summary of those parts of a number of the author's investigations which bear upon polarization and structure.

We have made a number of observations which seem to indicate that a definite relation exists between the structure of a deposited metal and its cathode potential. These observations have been recorded in detail in a series of papers[3] and we now wish to present a survey of the field as a whole.

I.

1. The more general facts that have to be taken into consideration have been collected by Foerster, and these are as follows: In order to deposit the metals of the iron group, *viz.*, Fe, Co, and Ni, a cathode potential is required that lies considerably above the potentials that these metals as such show in equilibrium with their salts. This indicates that the deposition of these metals meets with some kind of resistance. The phenomenon is most pro-

[1] Manuscript received June 1, 1923. Translated from the German by Prof. E. A. Vuilleumier, Dickinson College, Carlisle, Pa.

[2] Professor of Chemistry, University of Berne, Berne, Switzerland.

[3] Kohlschütter and Vuilleumier, Z. f. Elektrochem. **24**, 300 (1918).
Vuilleumier, Trans. Am. Electrochem. Soc. **42**, 99 (1922).
Stäger, Helv. chim. acta. **3**, 584 (1920).
Kohlschütter, Helv. chim. acta, **3**, 614 (1920).
Kohlschütter and Stäger, Helv. chim. acta, **4**, 821 (1921).
Kohlschütter and Schödl, Helv. chim. acta, **5**, 490 (1922).
Kohlschütter and Schödl, Helv. chim. acta, **5**, 593 (1922).

nounced in the case of nickel; our discussion therefore will be largely limited to this metal.[4] The abnormal polarization is highest at the beginning of the electrolysis and decreases gradually, without, however, reaching the theoretical value.[5] Immediately after breaking the circuit, the metal shows a less noble potential than that of nickel in equilibrium with the electrolyte; the difference gradually disappears, with the simultaneous evolution of hydrogen.[6] With rising temperature the over-voltage decreases and at 80-90° plating conditions are practically normal.[7] The polarization increases as the hydrogen ion concentration increases and passes through a maximum. The discharge of hydrogen ions therefore has an influence on the phenomenon, and it must be noted that more hydrogen is taken up by the metal in the early stages of deposition when the polarization voltage is highest than later when conditions have become more nearly normal.

2. In discussing the phenomenon it is important to compare the behavior of nickel with that of other metals. Here, too, abnormal deposition potentials are observed. Indeed, we may go so far as to say that the normal behavior is the exception; a statement which applies not only to the deposition of metals from complex salts or in the presence of colloids, but also to the deposition of metals from solutions of simple salts in which we would expect the reaction to be simply

$$M^{++} + 2 \ominus \leftrightarrows M$$

without any counter reaction.

In these cases it is generally accepted that the observed polarization may be due to two causes. First, that the electrode has been partly covered by adsorbed substances, which were an essential part of the electrolyte or which had been present as an addition agent. In consequence of this adsorption, a mechanical barrier is set up, the current density increases, as does also the electrode potential. The second cause of the rise in voltage is the depletion of the metal ions in the immediate vicinity of the cathode. The ions are liberated more slowly from their compounds than the current density demands.

[4] Förster, Abh. d. Bunsengesellschaft, 2, (1909).
[5] Förster, Z. f. Elektrochem. 22, 85 (1916).
[6] Schoch, J. Am. Chem. Soc. 41, 208 (1909).
[7] Schweizer, Z. f. Elektrochem. 15, 602 (1909).

3. These two causes, however, are not of primary significance in the case of nickel. Here the effect of abnormal polarization is much greater than in the case of other metals, and is largely independent of the nature of the electrolyte, whether composed of single or double salts.[8] The polarization of nickel must therefore be looked upon rather as a peculiarity of the metal itself. Furthermore, since the polarization voltage is affected by the simultaneous liberation of hydrogen (and this holds true for other metals, notably zinc) which in turn is affected by the condition of the surface of the cathode, the polarization is therefore dependent upon the condition of the surface of the cathode.

From these observations there seems to be no doubt that, at the moment of its deposition and immediately afterward, nickel metal exists under a stress, which stress is gradually relieved; and, secondly, that the hydrogen which is liberated simultaneously is accountable for the peculiar behavior. Finally, a fact worth noting is that the dissolution of the metal at the anode requires a potential considerably higher than the equilibrium potential.[7] We must not, however, assume that similar phenomena at cathode and at anode are necessarily due to the same causes.

II

The abnormal electro-potential phenomena of nickel cathodes are the more interesting and important since these phenomena are closely associated with abnormal forms of deposited nickel metal. Ordinarily metals are deposited from their simple salts in the form of individual crystals, or in distinctly crystalline layers. In order to get a fine-grained dense coherent deposit, we usually have to select a more complex electrolyte. Often this simply means the introduction of a colloid into the solution. It has been shown, for instance,[9] [10] that silver is deposited from a cyanide solution in a dense and smooth form because colloidal components, which are in equilibrium with the dissolved compounds, are deposited as an adsorbed film on the cathode and regulate the nucleus distribution. Such colloidal components, which form an integral part of the electrolyte, sometimes appear even in simple salt solutions as

[8] Förster and Blankenberg, Z. f. Elektrochem. **12**, 564 (1907).
[9] Kohlschütter, Z. f. Elektrochem. **19**, 181 (1913).
[10] Sand and Black, Z. f. phys. Chem. **70**, 496 (1909).

products of hydrolysis, and can then likewise give rise to a very fine-grained deposit.

When the structure of a deposit has been altered by substituting one electrolyte for another, we frequently notice a change in the deposition potential. However, this inter-relation does not always seem to exist. Some metals are deposited from certain electrolytes in which there is appreciable polarization in a form that is not essentially different from the form obtained from solutions giving normal potentials. On the other hand a change in structure is observed at times without any appreciable change in polarization. For example, it sometimes happens that merely a change of anion will change the structure of the deposit. The underlying cause in this case is probably merely an effect on the growth of the crystals and bears no direct relation to the actual electrode phenomenon, whereas in the previous case the change in structure is probably due to retardation in the supply of metal ions.

In the case of the metals of the iron group, and most strikingly in the case of nickel, we obtain, at ordinary temperatures and with simple salt solutions, dense, smooth deposits, sometimes even mirror-like, and, if at all granular, in very fine-grained layers; we do not observe the appearance of distinct individual crystals, so characteristic for other metals under the same conditions. This smooth deposit is obtained even in slightly acid electrolytes, in which we can scarcely expect colloidal decomposition products to exist and we must therefore attribute the structure to some other cause. The deposits show another peculiarity: during deposition a peculiar mechanical strain in the metal gives rise to the well known peeling of nickel deposits.

These internal stresses and the brittleness of the deposit are generally attributed to the hydrogen which the metal has taken up. In reality, however, as we will show later, the peculiar strain is the direct result of the highly dispersed structure of the deposit. The strain can be measured by means of a little apparatus designed for the purpose and which has been called a contractometer.[11] With the aid of this instrument it can be shown that the contraction is greatest in the early stages of the deposition, in other words

[11] Kohlschütter and Vuilleumier, Z. f. Elektrochem. 24, 300 (1918).

when the overvoltage is greatest; furthermore, that the contraction is a function of the nature of the electrolyte and increases as the hydrogen ion concentration increases.

The fact that with increased temperature a more distinctly crystalline deposit is obtained is further evidence of the parallelism existing between the structural and mechanical properties, on the one hand, and the polarization phenomena on the other. With rise in temperature the hydrogen content of the deposit decreases; the contraction and brittleness of the deposit become less pronounced. In other words, the same conditions that tend to eliminate the unusual structural and mechanical properties of the metal likewise tend to eliminate the abnormal polarization.

III.

On the basis of the above observed phenomena, we are led to conclude that a close relation exists between the specific structure of the deposit and the causes for the abnormal polarization. But how can we account for such a relation?

The answer may be sought in two directions. (1) There may be certain conditions which cause abnormal potentials and are directly responsible for the structure of the deposit; or else (2) there are primary causes responsible for the abnormal structure and this stucture in turn is responsible for the abnormal polarization. The problem as a whole can, therefore, be subdivided into three narrower questions:

1. What are the possible causes for the abnormal polarization?

2. How are we to interpret the morphological properties of the deposits?

3. Is it possible to discover a common cause for both potential and metal structure and in that way prove a relation between the two?

1. In attempting to explain the abnormal polarization of nickel it is important to bear in mind that the cause is to be sought not in the electrolyte but in the metal, as was indicated above. The structure or behavior of the metal may in turn, be due to the property of the metal atom or of the aggregation of the atoms, *viz.*, the solid phase. Therefore, considering the two factors

p and P which determine the equilibrium potential in the Nernst equation,

$$\epsilon = \frac{RT}{nF} \ln \frac{P}{p}$$

it is not a decrease in p but an increase in P which has caused the rise in ϵ.

In view of these deductions, let us first consider the theory of allotropy proposed by A. Smits.[12] According to his theory there exists in the metal phase as well as in the solution an equilibrium between metal atoms, metal ions and electrons, as follows:

$$M_s \leftrightarrows M_s^+ + \ominus_s \text{ and } M_L \leftrightarrows M_L^+ + \ominus_L$$

The individual components of these systems distribute themselves, each according to a definite ratio, between metal and solution. However, when a metal, for example nickel, is deposited on the cathode it is not necessary that the equilibrium in the solid phase

$$Ni \leftrightarrows Ni^{++} + 2 \ominus$$

should be established instantaneously.

On the contrary it is possible that the metal may at first exist with an excess of nickel ions and electrons. Consequently its potential will be above normal. The tendency of the nickel ions in the solution to be deposited is weakened by the higher concentration of the nickel ions in the metal, which is equivalent to a higher electrolytic solution pressure P for the metal. As is frequently the case with reactions in solid phases, the establishing of the e. m. f. equilibrium can be retarded by the presence of certain foreign substances taken up by the electrode; the effect of hydrogen, for instance, according to this conception appears to be that of a negative catalyzer.

A point in favor of this theory is that it will also explain the polarization of the nickel anode. As in the case of the cathode it was the slowing up of the reaction $Ni^{++} + 2 \ominus \rightarrow Ni$; so in the case of the anode it would be a slowing up of the reaction $Ni \rightarrow Ni^{++} + 2 \ominus$. The anode metal is deficient in ions and electrons as compared with the metal at equilibrium; and accordingly the dissolution potential of the anode will rise.

[12] A. Smits, Die Theorie der Allotropie, Leipzig, 1921.

On the other hand, Smits' theory offers no explanation for the structural peculiarities of the nickel deposit. The striking feature of the theory, however, is that it attributes the abnormal behavior of both electrodes to the metal itself, and this is in accordance with our own experimental observations. Essentially Smits' theory states that the nickel ions are present in the cathode in a higher concentration than corresponds with equilibrium conditions; in other words, that we are dealing with a case of supersaturation.

This explanation of Smits' is similar, perhaps, to that of Foerster[13] who suggested that nickel was primarily deposited as a hydride. As to the exact nature and composition of this hydride, Foerster draws no definite conclusions, but suggests that it may be a chemical compound or possibly a solid solution of hydrogen in nickel. Acordingly, the formula "NiH" which we use below has merely a qualitative meaning. The appearance of such a hydride in the cathode deposit would likewise correspond to a dynamic condition $NiH \leftrightarrows Ni + H$, and could thus cause nickel atoms of higher concentration than in the case of the pure metal to participate in the electromotive equilibrium, and therefore give rise to a higher solution pressure, P. The gradual decomposition of the hydride might well explain the gradual changes which take place not only in the polarization but in the hydrogen content of electrolytic nickel. The chemical changes occurring in the deposit would naturally give rise to structural changes, and these, in turn, to changes in mechanical properties.

The objection raised against the hydride theory is not a serious one, it being contended that we otherwise possess no proof or indications that a chemical compound or an alloy of nickel and hydrogen exists. Whatever may be the ultimate explanation, we must take into account the fact that the product primarily deposited on the cathode has a higher energy content than that of the product subsequently deposited.

We might be inclined to assume that the primary product is an unstable polymorphic form of nickel, but the differences in the potentials of allotropic modifications such as have been observed in the case of other metals, are very small and it is scarcely to be

[13] Z. f. Elektrochem. 22, 85 (1916).

expected that this would account for the large cathode overvoltages of nickel.

On the other hand we might safely consider the existence of intermediate products of high energy content that pass into the final crystalline phase. The existence of such products, notably those of a high degree of dispersion, we are almost compelled to recognize in view of the characteristic phenomena of metal deposition in general. Before we discuss more fully the interrelationship between these intermediate products and the deposition potential it will first be necessary to discuss briefly the second question suggested above: How are we to understand the morphological properties of the deposits?

Electrolytic metal deposition is a process of crystallization taking place on a surface. As is the case in every crystallization, the new phase grows out of a relatively small number of points. The form of the deposit depends primarily upon the ratio between the velocity with which nuclei are formed and the velocity with which nuclei already present grow into crystals. W. E. Hughes[14] has given a clear presentation of this problem, on the basis of his investigation of the structure of electrolytic iron.

Deposits of nickel are, as already mentioned, smooth and mirror-like, especially at the beginning, an indication that they are built up of very fine particles. The tendency of individual nickel crystals to grow is therefore slight; the discharged nickel atoms tend to form new nuclei, rather than to enlarge the nuclei already present. The metal covers the cathode, at the moment of its deposition, in the form of a more or less uniform film, made up of fine particles of colloidal dimensions.

It seems safe to assume that the structural elements of this film are crystals, even though not recognized as such under the microscope, since particles of colloidal metal solutions, produced in principle similar to that of the nickel deposits, are found to be crystalline when examined by x-rays.

Assuming that the metal did appear first in an unstable crystal modification, the change into the stable modification would increase the degree of dispersion even more; for every crystal which is present as a component of the first film would be replaced by a

[14] W. E. Hughes, On the Electrodepostion of Iron, Bull. 6, Dep. Sci. and Ind. Res., London (1922).

pseudomorphic aggregate of particles of the stable solid phase. Due to the fine state of subdivision, the primary deposit possesses an excess of surface energy as compared with that of the compact metal, and there is present therefore a tendency to decrease the surface. The crystals become larger, due to a crystal aggregation which is similar to the recrystallization of finely crystalline metal aggregates. This is the process that gives rise to the contraction of the films and, finally, to the peeling of the deposits, since it is possible to prove that the latter phenomena are associated with the formation of more coarsely crystalline aggregates.

The mechanical effects indicate that the forces that are active in the deposits are of considerable magnitude. In measuring the contraction of nickel deposits it is found that this contraction starts in at the moment of deposition. This indicates that changes in structure take place chiefly in very thin films. A metallographic investigation[15] has verified this conclusion; deposits which contract appreciably and those which do not show striking differences as far as their surface is concerned, but are essentially the same in their internal structure. In other words, after a deposit has contracted, it has the same structure as one which did not contract at all.

Since the quantity of metal in a surface film is very small, the excess of energy must be very large, and this again can only be explained by a high degree of dispersion. If, as has been observed, the degree of contraction decreases as the electrolysis proceeds and that the deposits take on a granular and crystalline appearance, this can be explained by the fact that after larger crystal aggregates have made their appearance, the newly discharged atoms find it easier to attach themselves to these rather than to form new aggregates. The experiments of Hughes, referred to above, show this clearly.

3. We are now prepared to give an answer to the third of the above questions. The nature and condition of the surface films fix the potential of the electrode. The large amount of free energy of the first greatly dispersed nickel films, which gives rise to the mechanical changes, must, therefore, also make itself manifest by an increased electrolytic solution pressure. This gives us

[15] Stäger, Helv. chim. acta. 3, 584 (1920).

the basis for showing the relation between the morphological and the electrochemical peculiarities which we meet in nickel deposition.

IV

Before we discuss this relation at greater length it will be necessary to bring up one more question: Why does not the nickel deposit after a time develop into large crystals so characteristic for other metals? Why is the deposit primarily restricted to structural elements of such small dimensions: that is, how is the development of the usual forms prevented?

1. It is a significant fact, as far as an explanation of the above is concerned, that a considerable overvoltage is required to liberate hydrogen on a nickel cathode. We, therefore, have to assume that a film of compressed hydrogen is also present on the surface of the cathode on which nickel is being deposited, since hydrogen ions are more readily discharged than nickel ions.

This film of hydrogen is the medium in which the metal deposition takes place, and this medium has an appreciable viscosity, since the hydrogen of the film is under considerable pressure. This film of hydrogen makes it difficult for the nickel atoms to combine into even small crystals, it hinders the development of larger crystals and the aggregation of smaller ones. We ascribe to the film of hydrogen, therefore, an influence which is similar in effect to that which absorption films of colloids exert in metal deposition. The effect which hydrogen has on polarization on the one hand, and its effect upon the structural and mechanical properties of nickel on the other, therefore, are due to a common cause, —a film of hydrogen. On account of this film the nickel is deposited in a highly dispersed form, which gives rise to the increased deposition potential as well as to the changes in structure.

If this relation exists then all conditions tending to strengthen the hydrogen film will tend to increase the deposition potential and to increase the degree of contraction of the deposit. On the other hand, conditions which are unfavorable to the formation of the film of hydrogen or tend to decrease the hydrogen over-voltage, will decrease the degree of dispersion of the nickel deposit and decrease the degree of contraction.

2. Experimental observations support these conclusions to a

considerable extent. We can now understand that with rise in temperature the polarization decreases and the deposit becomes more crystalline and contracts less, since the film of hydrogen, which is the cause of both, adheres less firmly at the higher temperature. On the other hand, an increase in the hydrogen ion concentration in the electrolyte increases the amount of gas liberated at the electrode. As long as there is no actual evolution of gaseous hydrogen, this film may increase considerably in thickness beyond that for equilibrium. After the gas begins to be evolved, however, the film takes on its normal properties. This explains why the polarization voltage, due to increase in the hydrogen ion content, passes through a maximum, and why nickel deposited from an electrolyte from which no hydrogen is being evolved during deposition, and in which the hydrogen charge of the electrode must therefore be considerable, shows a high degree of contraction. As soon as the gas begins to escape, the contraction becomes less and the deposit more granular.

In support of our above interpretation, we carried out a series of special experiments. Hydrogen depolarizers decreased, or even eliminated the structural peculiarities which manifest themselves in the contraction and in the abnormal deposition potentials; this fact seems to indicate that the role of the hydrogen is in accordance with our theory. First of all, chemical oxidizing agents act in this way. Especially striking results, however, were observed when an alternating current was superimposed. Its positive component counteracts the hydrogen gas polarization, and thereby reduces the thickness of the hydrogen film. The depolarization effect increased as the ratio of the alternating current to the direct current increased; the deposition potentials were brought down close to the normal values, and the metal deposited closely resembled other electrodeposited metals. Nickel deposits obtained with superimposed alternating current could be readily bent, while other nickel deposits without superimposed alternating current were brittle.

These experiments show that a general parallelism exists between polarization and the mechanical properties of the deposit, and that hydrogen plays an important part in both cases.

3. That the function of the hydrogen is that of bringing about

a highly dispersed metal film appears probable from another observation. Under certain conditions the characteristic tendency of the nickel plate to contract can be eliminated by removing the hydrogen; but, upon producing on the surface of the plate an adsorbed film of carbon dioxide, the plate will again tend to contract. To be sure, the deposition potential with the CO_2 film is lower than that for the hydrogen film, from which we conclude that the high hydrogen polarization potential is due to a higher degree of dispersion, probably of the first nuclei, than that necessary to bring about mechanical contraction of the plate.

Although the question of the abnormal polarization of nickel is by no means cleared up by the investigations here presented, I do believe that a discussion of the question from the viewpoint indicated above will be well worth while. I have not taken up at length the relation between anode and cathode polarization. If there is a direct connection between the phenomena at the anode and those at the cathode we may scarcely expect a proper interpretation until we know more about the relationship between potential and atomic structure.

SUMMARY.

1. The abnormal potential in nickel deposition bears a direct relation to the smoothness of the plate, the hydrogen content of the plate, and its tendency to contract and peel.

2. Factors which will affect one of these abnormal properties will affect the other two as well.

3. Eliminating the film of hydrogen gives rise to a more coarsely crystalline deposit; there is little or no contraction, and the abnormal polarization is largely eliminated. Substituting a film of carbon dioxide for that of hydrogen brings back the mirrorlike surface of the deposit and the tendency to contract, but does not bring back the abnormally high polarization voltage.

4. Under ordinary conditions, nickel is deposited in a viscous film of hydrogen and in a highly dispersed form.

DISCUSSION.

PER K. FRÖLICH[16]: The last part of the above paper is a short summary of an explanation of the process of electrodeposition of

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metals, first proposed by Kohlschütter and Vuilleumier in 1918, and since then frequently advocated by the author and his students with slight modifications in its presentation. The main feature of the hypothesis is a postulated hydrogen film on the cathode, acting as a dispersing medium for the metal initially deposited in a highly dispersed state. Originally the term, "colloidal metal," was used by Kohlschütter to characterize the intermediate state of electrodeposition. Fortunately, this term has been entirely abandoned since the idea of the colloidal state of metals has lost most of the significance and fascination, after x-ray examinations have shown that colloidal gold with an individual size as small as 1.86 $\mu\mu$ displays the same space-lattice as large crystals (Scherrer), and the same has been found to hold true for sub-microscopic tungsten powder prepared by reduction (Debye).

The data furnishing the basis of the hypothesis are obtained from experiments carried out on nickel deposition, using a so-called contractometer as a cathode, and the author claims (partly in this, partly in his original papers) that the observations made during these investigations cannot be explained without the assumption of a hydrogen film covering the cathode. It seems peculiar that Kohlschütter in this connection simply neglects the extensive and valuable researches of other investigators concerning the cathodic behavior of hydrogen. Foerster's hydride theory is mentioned in the paper, but no attempts have been made to apply it to the contractometer observations.

In trying to explain the phenomena in question as being due entirely to surface conditions, characterized by surface energy and postulated gas films, Kohlschütter's hypothesis is in apparent opposition to nearly all experimental facts obtained in studies of the different metal-hydrogen systems by other authors: Pd (Andrew and Holt, Harding and Smith), Pt (Foerster), Ni (Raoult, Foerster), Fe (Palmaer and Brinell, Foerster, Pilling), Zn (Schwarz, Palmaer and Wejnarth), as well as Sb, Bi and probably to a smaller extent most other metals are able to take up hydrogen when deposited together with this element or polarized cathodically in straight acid solutions containing no metallic cations.

Paneth and others have shown that hydrides of tin and other

metals can be isolated, when the metal in question is polarized cathodically. Raoult found that nickel was severely attacked when being cathodically polarized, using an acid as electrolyte. By repeated treatment the nickel cathode could be broken down even to a powder. In his studies of hydrogen overvoltage, Newbery observed pitting of the surface of all kinds of metals used as cathodes. These observations, of course, can not be explained as surface phenomena. Furthermore, Reichinstein has pointed out, and Pring has definitely proven, that the formation of gaseous hydrogen takes place in the cathode itself and not on the surface.

Various observations seem to indicate that hydrogen, when giving up its electrical charge, is taken up by the cathode in the atomic state. However, we do not yet know for certain whether it instantly combines with the metal to form hydrides (Newbery), or whether it first passes into solid solution or forms an alloy with the metal (Harding and Smith), or whether the dimorphic structure of the metal plays an important role (Andrew and Holt). Nor do the different investigators agree as to the mechanism of the reactions leading to evolution of gaseous hydrogen (Newbery, MacInnes). What we do know is that metals are able to take up a certain amount of hydrogen, palladium and nickel even several hundred times their own volume, and that they also do so when being cathodically polarized. An attempt to explain the cathodic behavior of metals, especially nickel, as being due entirely to surface phenomena naturally fails to serve the purpose.

In choosing nickel for his investigations, Kohlschütter has limited his observations to the metal which, next to palladium, shows the most peculiar behavior towards hydrogen. The tremendous activity of nickel as a catalyst, in all kinds of hydrogenation reaction, places this metal in a specific position among other metals. Hence, it does not seem logical to deduce a hypothesis of cathode reactions on observations made with nickel, and a generalization of the hypothesis to cover other metals is not at all justified.[17]

Professor Kohlschütter's hypothesis requires an enormous rate in the process of recrystallization.[18] Crystallographic and metallographic investigations fully prove that such an instantaneous

[17] In his original papers, Professor Kohlschütter states that the hypothesis concerns all kinds of metals.

[18] In an earlier paper this phenomenon was called coagulation.

recrystallization cannot take place at room temperature (Tammann, Podzus).

The postulated hydrogen film is said to be of considerable viscosity, and it certainly would have to be of considerable thickness, too, since it is assumed to act as a dispersing medium from which periodical coagulation or recrystallization takes place when supersaturation occurs.[19] The thickness required would not be conceivable with our knowledge of the dimensions of adsorbed films.[20] However, even if considerable electrostatic forces are assumed to account for the existence of this abnormally dimensioned film, how can the film conception explain the quiet gas evolution observed at a working cathode? Is it physically possible that, on the surface of a "highly compressed gas film of considerable viscosity," bubbles of nearly atmospheric pressure can be gradually built up and escape, leaving nuclei for the next bubbles to form, as was observed by MacInnes?

Some time ago I studied Kohlschütter's work carefully in connection with some investigations on the effect of colloids on electrodeposition. I collected about 20 more or less characteristic contractometer observations from the various papers, and found that in no case did the hypothesis offer any better explanations than those which can be deduced from our present interpretation of the metal-hydrogen system, involving hydrides, alloys or solid solutions. Furthermore, it appeared to me that the very proof against the hypothesis is to be found in Kohlschütter's own observations. The limited time will not allow a detailed discussion of these points, but I would like to mention just one of the observations: When the nickel-plated contractometer was cathodically polarized in an electrolyte containing only hydrogen as cations, the contraction was eliminated, that is, the bent platinum foil was stretched out to its original plane condition. Does not this indicate that hydrogen enters the metal and gives rise to the forced conditions existing whenever hydrogen is present in a cathodic deposit? Or, does it seem more reasonable to accept Professor Kohlschütter's explanation that "hydrogen is pressed on to and into the deposit causing the nickel to go back to the disperse phase"?

Besides the contraction phenomena, the film hypothesis claims

[19] Statement taken from Kohlschütter and Vuilleumier's original paper.
[20] See Bancroft's "Applied Colloid Chemistry" for detailed data.

to account for the abnormal potentials observed in nickel deposition. It is interesting to note that similar irregularities in deposition potentials are observed in the case of simultaneous deposition of nickel and zinc as in the case of nickel and hydrogen. Does zinc here play the role of the hydrogen film in the latter case "as a dispersing medium for the initially deposited finely disperse nickel?"

The mechanism of cathode reactions is one of the most interesting questions in electrochemical research today. What we want to find out is the mechanism of the reaction:

$$\text{metallic ion} + \ominus \rightarrow \text{crystalline metal}$$

Without stating that future research may not change our view, it may be said that up to the present time there are no indications whatever of intermediate steps in the cathode reaction, be it a formation of hydrated ions, hydrated atoms, colloidal metal or highly disperse metal. The simplest explanation of the phenomena is still the best one.[21]

The metals of the iron group are generally deposited in a finer crystalline state than other metals under similar conditions. No doubt, this is mainly due to the peculiar behavior of these metals in their simultaneous deposition with hydrogen. The effect of hydrogen will in all probability have to be sought in the disturbing influence exerted by this element on the process of building up the normal space lattice of the crystalline metal, rendering the deposit so brittle that it may even be crushed with the fingers (as is observed, for instance, in the case of zinc).

When hydrogen escapes from this forced condition, the crystalline forces will tend towards equilibrium; hence the contraction of the deposit. This is not a simple recrystallization from a pseudomorphic to the normal structure, as Kohlschütter's hypothesis demands, and which seems improbable at room temperature. An explanation such as the one suggested here would also be able to account for the abnormal potentials observed not only when hydrogen, but also when metallic cations, are co-precipitated with the metal in question. There are good reasons to believe that many of the present problems in electrodeposition

[21] Compare Blum and Rawdon, Trans. Am. Electrochem. Soc., 44, 305 (1923).

will not be solved except by crystallographic and metallographic methods in the research.

A. K. GRAHAM[22]: Professor Kohlschütter's paper is a splendid one. He includes in his discussion of the mechanism of metal deposition and of abnormal potentials the idea of Smits regarding the possibility of allotropy. The variation of the potential of nickel deposited under various current densities is usually explained by differences in the structure of the deposit, the quantity of gas absorbed, etc. Cohen in his work on allotropy has obtained allotropic forms of metal by electrolytic methods, and in doing so particular attention was paid to the current density. We ought to include the idea of allotropy in a discussion such as the author presents.

H. E. HARING[23] (*Communicated*): In a series of nickel anode potential measurements recently carried out at the Bureau of Standards, I noticed that maximum polarization occurs practically at the beginning of electrolysis. The author states that a similar phenomenon takes place at the cathode in nickel deposition. My observations in connection with a series of nickel cathode potential measurements now in progress are in accordance with this statement. The author attributes this cathodic phenomenon to the difficulty in instituting bubble formation. This seems quite logical. It also seems warranted in the case of the anode.

Personally, I am of the opinion that the abnormally high polarization at nickel electrodes is due to the formation of gas electrodes. At the anode (providing passivity exists) we have to deal with the oxygen electrode; at the cathode, with the hydrogen electrode. If this view is correct, it might be possible to use the potentials of such electrodes as a measure of the hydrogen ion concentration at the electrode-solution interface.

C. P. MADSEN[24] (*Communicated*): Observation of large scale commercial electrolysis leads one to believe that anode and cathode reactions are more independent of each other than indicated by former theories. I therefore think that the type of studies which this paper gives of these phenomena will add much to our knowledge. The absence, however, of micro-photos of actual structures,

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[23] Assoc. Chemist, Bureau of Standards, Washington, D. C.
[24] Consulting Engr., New York City.

together with a lack of analyses of solutions and anodes, does not permit of final conclusions.

The theory of the dynamic condition of the nickel itself in the solid phase being a factor in controlling its physical condition when electrodeposited, is worthy of further investigation. In conformity with the electronic theory of the structure of matter, the fact that the atomic weight of nickel contains a fraction indicates that it is isotopic, and a change from one isotope to another can clearly free electrons. Further light may be thrown on this with relation to electrolysis by an investigation of the separate film phenomenon. It is well known that if nickel deposition be interrupted, as by breaking the circuit, or by lifting the cathode from the bath, a separate layer will form upon returning. I have found that this action takes place upon the exposure of the cathode for from ten to fifteen seconds almost regardless of other conditions. It would seem that any hydrogen present would escape in less time than this, and that no appreciable oxidation can take place.

The "high pressure hydrogen film" explanation throws some light on the behavior of nickel cathode, but it is not clear, nor does anything else in the paper explain clearly why the tendency for the cathode to contract diminishes as the thickness increases. May it not be possible that molecular forces of the material upon which the deposit is made affects the nickel deposit initially, diminishing as the deposit grows in thickness beyond the range of these forces? It is at any rate true that the degree of adherence of a nickel deposit, particularly upon steel, undergoes a sharp change when the deposit reaches a thickness about equal to that of one crystal layer of the steel.

The author does not state whether his solutions were chemically pure or commercial, nor does he give the analysis of his anodes. If commercial materials were used they certainly contained both iron and organic matter. I have found, as discussed in my paper,[25] that small traces of iron have an enormous influence upon the character of the nickel deposited, and since iron is deposited at a slightly lower e. m. f. than nickel, may it not be possible that the deposit contains initially more iron than subsequently, and hence absorbs more hydrogen and contracts more. Traces of organic material have the same tendency.

[25] This volume, page 249.

It is possible, therefore, that if this work were to be repeated using new electrolytes absolutely free from every trace of iron and organic matter, slightly different conclusions might be reached.

The conclusion that practical improvements can be obtained by introducing oxidizing agents in the bath is unwarranted. Thompson, in discussing my paper,[26] reports negative results. During 1920, I made a number of experiments, results of which agreed with Thompson's, with the exception of hydrogen peroxide and some persulfates, which are reported in the paper mentioned above. The use of superimposed alternating current has not been found practicable in commercial work.

[26] Trans. Am. Electrochem. Soc., 39 483 (1921).

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

MECHANICALLY PERFECT ELECTROLYTIC NICKEL.[1]

By Charles P. Madsen.[2]

Abstract.

Ordinary electrolytic nickel is brittle and often mechanically imperfect. Furthermore, ordinary electrolytic nickel tends to become cold short. Theoretical discussion is omitted, and instead statements are limited to empirical results obtained. Hydrogen alone is not the principal cause of electro-nickel trouble. Organic material and iron are far more important, and their effect depends upon their condition. Soluble organic material is the principal cause of lack of ductility. Organic colloids cause failure after heating the metal, and larger organic particles enter into pit formation during cathode deposition. Means are described for producing electro-nickel almost equal to pure gold in ductility. The use of hydrogen peroxide in the bath is claimed to be an absolute cure for pits, and exerts other beneficial effects. An anode is described which gives consistently good results in the above bath. [C. G. F.]

In a former paper[3] I disclosed a new method of making a highly ductile nickel, but intimated that better results were obtained on large scale operations by the use of an addition agent and a new anode, neither of which I was then at liberty to disclose. The addition agent referred to is hydrogen peroxide, and the anode may be briefly described as to consist of the eutectic of tri-nickel carbide and pure nickel.

[1] Manuscript received April 3, 1924.

[2] Consulting Engineer, New York City.

[3] Trans. Am. Electrochem. Soc., 39, 483 (1921).

I. COMMON DEFECTS OF ELECTROLYTIC NICKEL.

The common defects of ordinary electrolytic nickel are:

1. Lack of ductility.
2. Presence of "carbuncles."
3. Failure after annealing.
4. Presence of pits.

The last two are related, and are by far the most difficult to overcome.

Ductility. Lack of ductility is caused principally by soluble organic compounds in the bath, although hydrogen and iron are also factors under certain conditions. All commercial nickel salts contain organic matter; furthermore, open tanks will be exposed to the organic dust of the atmosphere; finally, greasy or oily cathodes, not properly cleaned, will introduce organic compounds into the solution. Less than one part in a million of soluble organic material will affect the degree of ductility of the deposited nickel; even 10 mg. per L. of some organic substances will make the metal very brittle. Practically all of the organic matter can be completely removed or destroyed by chlorination; the effect of small amounts is inhibited by hydrogen peroxide.

The relative quantity of hydrogen generated is a function of the electrolyte temperature with relation to current density and acidity; and the amount absorbed by the cathode is a function of the temperature with relation to the amount of iron that is co-deposited with the nickel and the amount of soluble organic material in the bath. The co-deposition of hydrogen diminishes so rapidly with rise of temperature that at about 60° C. electrolytic nickel having a ductility at least equal to that of copper can be produced from an electrolyte which is *free from organic matter,* but whose composition, temperature, electrodes, etc., may otherwise vary within wide limits. On the other hand, such nickel may, however, be so afflicted with any or all three of the other defects that its only commercial use would be for making nickel alloys by melting.

"Carbuncles." "Carbuncles" are caused by floating or suspended insoluble particles somewhat above colloidal size, and their formation is aggravated by too high a current density. Cutting down the current helps only temporarily, because particles falling

into the vat from the air and accumulating from decomposition of commercial anodes will soon reach a concentration at which "carbuncles" will form even at low current densities. The apparently obvious remedy of continuous filtration is not so easy to apply as would appear. Impure commercial nickel salts and commercial nickel anodes require the presence of nickelous hydrate in the bath. Any filtration employed to prevent "carbuncles" will also remove this hydrate, resulting in cathode metal which is highly pitted, and which will fail after heat treatment. Bags or diaphragm cells are only partially effective, because soluble ferrous salts will readily hydrolize and oxidize after passing through the diaphragm. The practical remedies are to be sought in the use of very pure anodes, and by either keeping the bath covered or by working in a dust proof room.

Failure after Annealing. Nearly all electrolytic nickel now made, even that which is partly ductile, will become "cold short" after heating above a red heat, whether it has been mechanically worked or not. For instance, it may initially have a Brinell hardness of only 90 to 100, and a ductility nearly equal to that of copper, but if heated to above a red heat its ductility will drop to below that of cast iron without change in hardness. The best of such nickel metal may be mechanically worked to an extent far greater than that of any other common metal without embrittlement, although its Brinell hardness may increase to 183; but if it be afterward heated above a red heat, both its ductility and tensile strength will drop far below the original, even though its hardness may be reduced to the original figure. Such metal has limited industrial applications and its use may be seriously objected to in some cases.

The cause of this "cold short" phenomenon is the deposition of true colloids on intercrystal facings, which probably enlarge upon heating, thereby rupturing the crystal bondage. These colloids are, in the order of their importance, ferric hydrate, organic colloids, colloidal graphite and insoluble lead salt colloids. The obvious remedy is to avoid the formation of any trace of these colloids in the bath, but this is commercially impractical at present. Neither ordinary filtration nor the supercentrifuge will remove all

of them. They can, however, be agglomerated or depeptized and then removed by ordinary filtration.

Pitting. This defect has been by far the most difficult to overcome of all defects of electro-nickel. Pits are produced by the catalytic action of a fine foreign particle at one or more points on the face of the cathode, causing the formation of, and discharge of, atomic hydrogen at that point or points, the metal deposits around the hydrogen stream, forming a deep well with a concave mirrored bottom. There are apparently at least two principal classes of these fine particles—living organisms and ferric compounds. Our tests indicate that there are several ferric compounds which can act in the above way, but their exact nature is not known.

Soluble ferric salts can cause this pitting trouble, but there is evidence that other less soluble ferric compounds will form from these salts, which will increase the pitting. One of these compounds is probably a hydrated ferric oxide, but the worst one seems to be an oxychloride. It has been impossible to determine their exact nature, since not enough material has been available; it takes less than one part in a million of the bath to cause pits.

It has been equally impractical to prevent the generation of sufficient hydrogen to produce at least one pit if one catalyst particle be present, and to prevent the formation of at least one catalyst particle on the cathode by any amount of practicable filtration; and a single pit is sufficient to ruin an otherwise perfect cathode.

Addition of Hydrogen Peroxide Eliminates Pits.

The introduction of small amounts of hydrogen peroxide into the bath has been found to be an absolute remedy for pits and most ills of electrolytic nickel.

This effect was discovered through the discrepancies in obtaining electro-metric pH readings, which have also been reported upon by Blum.[4] It was noted that such readings made on a new bath of known acid content checked fairly well with one another, but that such a bath always produced many pits on the cathodes. After long continuous operation of the bath, pH readings no

[4] Trans. Am. Electrochem. Soc., 39, 466 (1921).

longer checked among themselves but the number of pits produced diminished, in spite of the evident increase in impurities in the bath, which were known to enter into the pit-forming mechanism. The pH values were checked by the iodate method, and by the known pH values at which ferrous and nickelous hydrate respectively balance. Boiling the test sample raised the pH reading materially.

This indicated that something was formed by electrolysis which diminished pitting and which discharged the hydrogen electrode, but was decomposed by boiling the sample to a condition which affected the hydrogen electrode less. Our analyst reported finding faint traces of persulfates or hydrogen peroxide in sulfate electrolytes after electrolysis. When a few drops of 3 per cent H_2O_2 were purposely added per liter of a new bath, the same high grade metal was produced, and the same pH reading obtained, as that obtained from a long used nickel plating bath. Larger amounts of H_2O_2 were found absolutely to prevent the formation of any pits, regardless of the amount of impurities present in the bath. These impurities may, nevertheless, cause any of the other nickel diseases or defects. The presence of the peroxide brings about other valuable results, the reasons for which are not all yet known. One valuable result is that the size of ferric hydrate colloids seems to enlarge, so that these can be filtered out and thus remove one of the causes of failure after annealing.

Many other known oxidizing agents were tried, but none was found to be as beneficial as H_2O_2, and nearly all of them directly or indirectly caused other troubles.

II. PRODUCTION OF PERFECT ELECTROLYTIC NICKEL METAL.

Iron Mechanism. From the results outlined above, we are led to conclude that iron plays an important part in the causes of all the electrolytic nickel diseases, and that the quality of the cathodic product obtained depends upon the chemical and physical condition of the iron compound present in the bath. We may summarize as follows: Ferrous hydrate is highly beneficial, tending to produce smooth cathode metal and to diminish pitting, but it can not be maintained in this ferrous condition for any length of time. Ferric hydrate, in colloidal form, causes failure after

annealing, and in agglomerated form in the bath causes "carbuncles." Soluble ferrous salts obviously permit the deposition of metallic iron, forming a ferro-nickel alloy, which absorbs more hydrogen than the pure nickel, and is therefore harder and much less ductile. Soluble ferric salts enter into the mechanism of pit formation. To produce mechanically perfect electrolytic metal, it is therefore necessary either to maintain the chemical compound of iron, such as ferrous hydrate, in its original beneficial form, or to eliminate the iron entirely from the bath. The latter scheme is the more practical.

Purifying the Electrolyte. Chlorination in the presence of nickel hydrate destroys organic material, and removes all of the copper and nearly all of the iron. The last trace of colloidal ferric hydrate may be removed by heating the bath slowly with a fresh charge of nickelous hydrate and hydrogen peroxide, and then filtering. If this bath could now be operated sealed and an absolutely pure nickel anode employed, no trouble would be experienced in making perfect cathode metal. But such a procedure is at present commercially impracticable.

Anodes. Absolutely pure nickel does not become passive under electrolysis as has been reported by others in the past. The passivity effect observed is due to traces of Cr, Mn and Si in the nickel, together with the variable areas of variable small oxygen content. These impurities are present in nearly all commercial nickel, and even the best rolled malleable nickel contains both manganese and oxygen.

In the carbon eutectic anode referred to above, all metallic impurities have been removed, except a mere trace of iron, and the total absence of oxygen is insured by the high carbon content. But unless this anode is made with extreme care there will be free graphite present, which will cause trouble during subsequent electrodeposition.

Strange to say, the extreme opposite practice with regard to oxygen also applies; that is to say, if all traces of the injurious metallic elements have been removed, then an extremely high oxygen content will aid solubility of the anode. But such an anode may throw off colloidal particles of metallic nickel and of Ni_2O_3.

It has, however, now become possible to make an anode at a comparatively low cost which is absolutely free from oxygen and contains none of the injurious metallic elements, excepting a small percentage of iron. This is, therefore, the best practical anode to use. At present it is not commercially feasible to reduce the iron content below one-quarter of one per cent, but perfect electro-nickel can be made with this anode continuously by the use of H_2O_2 in the bath, as described above.

Operating Factors. Using Dr. O. P. Watts' bath[5], purified as described above and kept at 55° C. (130° F.) with a current density of 36 amp. per sq. ft. (4 amp. per sq. dm.) and with the last described anode, the addition of 1 to 4 cc. of a 3 per cent H_2O_2 solution per L. of bath initially, and then 4 cc. every 24 hr. of operation, insures absolute freedom from pits. Under these conditions accurate pH control is not necessary, provided the pH is kept well on the acid side. Its value may be lower than formerly supposed to be, but this may be accounted for by the fact that the value is somewhat dependent upon the actual H_2O_2 concentration. A pH between 3 and 6.8 is permissible, but pH 6.2 to 6.6 is to be preferred, as the removal of ferric salts is facilitated under these conditions.

Good nickel metal can be produced at from 20 to 144 amp. per sq. ft. (2 to 15.5 amp. per sq. dm.), but 36 amp. per sq. ft. (4 amp. per sq. dm.) corresponds to the thermal balance under usual commercial operating conditions. If the bath is operated without agitation and filtered every 24 hr., the metal will be about equal to that of poor brass, but if continuous filtration be used an electrolytic nickel can under the above conditions be deposited up to one inch in thickness, free from all carbuncles and pits, and which will have a ductility both before and after annealing nearly equal to that of pure gold.

CONCLUSIONS.

1. Perfect electrolytic nickel can be produced from a bath containing absolutely nothing but nickel salts and a little free acid, by using an anode containing absolutely nothing but nickel.

2. Perfect electrolytic nickel can be produced from a bath made

[5] Trans. Am. Electrochem. Soc., 29, 396 (1916).

from commercial nickel salts and using an anode low in iron, but otherwise pure, by the use of hydrogen peroxide in the bath.

3. Accurate pH control is made necessary only by the presence of iron.

4. In the deposition of nickel from aqueous electrolytes a high bath temperature is necessary for best results.

5. The cause of "carbuncles" is suspended impurities in the electrolyte above colloidal size.

6. Organic material is the chief cause of brittle or otherwise poor nickel deposits.

7. Under proper conditions nickel metal can be electrodeposited having a ductility approaching that of gold.

My research on electro-nickel has extended over a period of about eight years. During this period valuable suggestions and encouragement were received from Messrs. Fred. G. Cottrell, Colin G. Fink, J. W. H. Randall, Wm. Blum and George B. Hogaboom.

DISCUSSION.

S. SKOWRONSKI[6]: Mr. Madsen's paper is an important one. If there is any soluble organic matter in the electrolyte, there is no question about it getting into your cathode deposit. *Chromium* also has a peculiar effect on a nickel deposit. Even in the electro-analysis of nickel in an ammoniacal solution, the presence of chromium prevents the complete deposition of the nickel, making it impossible to obtain an accurate determination of nickel by the method of electrolysis.

A. K. GRAHAM[7]: Is Mr. Madsen at liberty to say how he would treat an iron or steel surface in order to prevent porosity when it is plated with nickel?

C. P. MADSEN: I intended to disclose it completely at this meeting, but I would rather not say anything about that now as our work along that line is not yet completed. However, I expect to have a paper ready for the next meeting.

[6] Research Chemist, Raritan Copper Works, Perth Amboy, N. J.
[7] Chemical Engr., Philadelphia, Pa.

M. R. THOMPSON[8]: I have recently been electrolyzing a nickel chloride solution in which basic nickel carbonate was suspended. The anodes were platinum, and there was an evolution of chlorine at them. Under such conditions, a very finely divided black substance was formed in suspension which appeared to be a nickelic compound. In connection with the statement about chlorination, on page 254, has Mr. Madsen ever noticed the formation of a black nickelic compound.

C. P. MADSEN: The black compound usually indicates that chlorination has been carried too far, and in this case consists mostly of cobalt and iron. Excessive chlorination of a hot nickel solution can also form complex oxygen nickel compounds, containing even some Ni_2O_3.

M. R. THOMPSON: I refer to a case where copper, iron and cobalt were all absent.

WM. BLUM[9]: In your discussion of anodes you refer to the benefit of using a practically pure nickel anode, that is, 99.75 per cent nickel. In your paper, you mention (page 249) the eutectic of nickel and carbon, presumably containing 2 per cent carbon. Have you a decided recommendation for either one of these compositions?

C. P. MADSEN: The last anode named is essentially a malleable cast pig of the same nature as that which is cast for making rolled anodes, with this difference that in our case a new method of deoxidizing is used, together with refining methods, which eliminate injurious metallic impurities, and the absorption of further oxygen is avoided by omitting hot rolling.

PER K. FRÖLICH[10]: Cannot much of the trouble with these so-called organic colloids be avoided by using some kind of a diaphragm, for instance, simply by surrounding your anode with a cotton bag? At least a part of the impurities might be removed by a diaphragm or a filter.

C. P. MADSEN: The particles are of all sizes.

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[9] Chemist, Bureau of Standards, Washington, D. C.
[10] Research Assistant, Mass. Inst. Technology, Boston, Mass.

PER K. FRÖLICH: Could you eliminate the coarsest particles?

C. P. MADSEN: Yes, but the result would be about the same as if you took precautions with a human being as to whether he got 1 or 50 g. of strychnine. The smallest trace does just as much damage as a very large amount, except in the degree of roughness. Another reason is that a part of the colloids are formed from the soluble components themselves, and these will go through any diaphragm that would operate.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

ACIDITY OF COBALT AND NICKEL PLATING BATHS. USE OF THE OXYGEN ELECTRODE.[1]

By G. H. Montillon[2] and N. S. Cassel[2].

Abstract.

A possible explanation is given for the failure of the hydrogen electrode in the direct measurement of hydrogen ion concentration of nickel and cobalt plating baths. The oxygen electrode gives approximate hydrogen ion concentration values, which are useful for controlling acidity in these solutions. For the plating baths used a pH of 6 gave the best current efficiencies and the most desirable plates. Further work is needed to establish the accuracy of this method.

INTRODUCTION.

One of the important factors in the successful plating of cobalt or nickel is the acidity, or hydrogen ion concentration of the plating bath. H. T. Kalmus[3] in an extensive study of cobalt plating, made up a series of sixteen baths and studied their characteristics. However, no attempt was made to measure the acidity of the baths, except to note that they were "acid" or "basic" to litmus. M. R. Thompson[4] in his work on "The Acidity of Nickel Depositing Solutions" conducted a series of experiments to determine the proper acidity of solutions for nickel plating, using the L. J. Gillespie drop ratio colorimetric method for obtaining the hydrogen ion concentration. He has shown this to be a reliable means of defining the acidity characteristics of such solutions.

[1] Manuscript received July 2, 1923.

[2] Chemical Engineering Labs., University of Minnesota, Minneapolis, Minn.

[3] Electroplating with Cobalt. H. T. Kalmus, Trans. Am. Electrochem. Soc. **27**, 75 (1915).

[4] The Acidity of Nickel Depositing Solutions. M. R. Thompson, Trans. Am. Electrochem. Soc. **41**, 333 (1922).

Wm. Blum[5] in an article on "The Use of Fluorides in Solutions for Nickel Deposition" says that, for some reason, the direct use of the hydrogen electrode does not give reliable results when used to measure the acidity of nickel baths. J. A. Reinhardt, of the Western Clock Company, has stated in a private communication that they had made a number of measurements of the acidity of their nickel plating baths with the hydrogen electrode, but they were not able to check their results. The same trouble was encountered in our laboratory.

It was thought, however, that if it were possible to determine the reason for this peculiar behavior of the hydrogen electrode and to correct it, a direct electrometric method would be of value for this work.

EXPERIMENTAL.

It is known that the acidity of solutions containing the alkali or alkaline earth metals, as salts of organic or inorganic acids, may readily be determined. Such metals are far above hydrogen in the electromotive series. For solutions of the metals close to, or below hydrogen, little is known, but the work on nickel plating solutions would indicate that some unknown factor was interfering. Wm. Blum[5] says that the presence in commercial solutions of small amounts of copper, iron or arsenic, may "poison" the electrodes, but the difficulty when using pure nickel sulfate can not be readily explained.

To obtain data on the behavior of the hydrogen electrode in the presence of such metallic ions near it in the electromotive series, a solution of normal copper sulfate (A), and solutions for nickel (B) and cobalt (C) plating were made up, and tested, using an ordinary potentiometer method to obtain the single potential of the hydrogen electrode against a normal calomel electrode.

The following results were obtained, using +0.56 as the value of the calomel electrode against the "absolute" zero of potential:

A. Normal copper sulfate at 20° C. $E_a = +0.571$, where E is the single potential on the absolute scale. In this case the hydrogen electrode acts very nearly like a copper electrode, which on the absolute scale has a potential of +0.58 in normal copper sulfate solution.

[5] The Use of Fluorides in Solutions for Nickel Deposition. Wm. Blum, Trans. Am. Electrochem Soc. 39, 459 (1921).

B. Nickel plating bath. Nickel sulfate, 140 g./L.; nickel chloride, 12 g./L.; boric acid, 16 g./L.

Results at 22° C.

Cell	e. m. f.	Single Potential
(a) Hydrogen electrode-calomel.....	0.382	$E_a = +0.178$ for H_2
(b) Nickel electrode-calomel.....	0.295	$E_a = +0.265$ for Ni.

Therefore the hydrogen electrode was 0.087 v. more negative than the electrolytic nickel electrode in this bath.

C. Cobalt plating bath. Cobalt sulfate, 312 g./L.; sodium fluoride, 14 g./L.; boric acid, nearly to saturation.

Results at 22° C.

Cell	e. m. f.	Single Potential
(a) Hydrogen electrode-calomel.....	0.600	$E_a = -0.040$ for H_2.
(b) Cobalt electrode-calomel.....	0.442	$E_a = +0.118$ for Co.

Therefore the hydrogen electrode is 0.158 v. more negative than the electrolytic cobalt electrode in this bath.

It is evident that in the copper sulfate bath the hydrogen electrode ceased to function as such, and acted much like a copper electrode. In the nickel plating bath the e. m. f. of 0.382 would indicate a pH value of about 1.7, a value extremely low according to the work of Wm. Blum[5] and M. R. Thompson[4], who found that similar baths had a pH of about 5.8.

As the values for the single potentials showed that the nickel and cobalt electrodes were more positive than the hydrogen electrode in these plating baths, it would seem reasonable to assume that the "poisoning" of the hydrogen electrode in these instances, as well as in the case of the copper, may be due to the tendency of these metals to deposit on the hydrogen electrode used, so that the hydrogen electrode ceases to function as such, but acts rather as a metallic electrode according to the metal deposited.

The reason for the position of hydrogen in the electromotive

series is often misinterpreted. For the hydrogen electrode at 25° C., we have according to the Nernst formula[6],

$$E_a = + 0.277 + 0.0591 \log C_{H^+}$$

This equation shows that E_a becomes more negative with decreasing hydrogen ion concentration. At a low concentration of hydrogen ion with pH equal to 6, E would become —0.078, so that it is easily seen how the potential of the hydrogen electrode in such a solution might easily become more negative than the potential of the nickel electrode.

In the light of this evidence, it seems reasonable to state that the hydrogen electrode can not be used for measuring the pH of solutions whose metallic ions are usually below hydrogen in the electromotive series, or in solutions whose ions are below hydrogen due to changes in electromotive force brought about by changes in the respective ion concentrations, of hydrogen and the metals concerned.

The work of N. H. Furman[7] on the oxygen and air electrodes showed that they could be used for electrometric titrations and that they gave approximate hydrogen ion concentration values. Since the trouble with the hydrogen electrode as used with nickel and cobalt plating baths was the danger of "poisoning" due to a possible metal deposit or coat, it was assumed that if an electrode could be found that would vary with the hydrogen ion concentration, and which at the same time would be more positive than the single potential of the metal present in the solution of which the hydrogen ion concentration was being measured, the danger of "poisoning" would be eliminated and consistent results would be obtained. The preliminary experimental work done on this paper would indicate that this is true for the oxygen electrode. Additional work is being carried on with both the oxygen and air electrode for both nickel and cobalt plating solutions.

The fact that the air electrode is not "poisoned" in the presence of copper and iron is shown by the experience of Tilley and Ralston[8], who stated that they had been using the air electrode

[6] Applied Electrochemistry, Allmand, 1920 Edition, p. 98.

[7] Some Applications of the Oxygen Electrode, N. H. Furman, J. Am. Chem. Soc. 44, 2685, (1922); and Trans. Am. Electrochem. Soc. 43, 79 (1923).

[8] An Electrometric Method of Following Certain Inorganic Hydrolytic Reactions. G. S. Tilley and O. C. Ralston, Trans. Am. Electrochem. Soc. 44, 31 (1923).

for some time and had found it satisfactory in following the purification of inorganic salts, such as copper sulfate or zinc sulfate. In the case of a solution of copper sulfate plus ferrous sulfate, as soon as the point is reached where most of the ferric salt is hydrolyzed, a distinct kink in the voltage curve is noticeable. For this purpose the air electrode has been more reliable than the hydrogen electrode; and straight chemical methods are unsatisfactory. In the elimination of iron from aluminum sulfate, the air electrode has been an indispensable piece of apparatus.

CALIBRATION OF THE OXYGEN ELECTRODE.

In discussing the theory of the oxygen electrode N. H. Furman[7] says, "For any given solution of an oxidizing agent, which is in contact with a platinum electrode, there will result a balance between the tendency of the substance to evolve oxygen and the opposing pressure of the oxygen which is dissolved in the electrode. We may regard this process from the standpoint of the oxygen ion. Oxygen dissolved in the electrode tends to ionize in proportion to its partial pressure, the electrode becoming positively charged. $O_2 \leftrightarrows 2O^{=}$, at constant temperature, $\frac{[2O^{=}]}{[O_2]} = K_1$. This tendency is opposed by the osmotic pressure of the oxygen ions of the solution, which is constant at any given temperature. For any given solution at constant temperature the concentration of the oxygen ions is defined by the relation:

$$[O^{=}] = \frac{[k'\,k'']}{[H^{+}]^2} \text{ (since } [H^{+}][OH^{=}] = K'' \text{ and } O^{=} + H^{+} \leftrightarrows OH^{-})$$

and hence at equilibrium, $\frac{[O^{=}]\,[H^{+}]}{[OH^{-}]} = K$.

"The electromotive force which is developed by a cell composed of such an electrode, together with a normal calomel electrode, will be a function of the oxygen ion concentration of the solution. The concentration of oxygen ions will be dependent both upon hydrogen ion concentration, and that of oxidizing agent. If we keep the latter concentration constant we should expect a sharp inflection in the electromotive force-hydrogen ion concentration curve as we pass the neutral point. Such an inflection is experimentally realized in all the cases the author has been able to test."

Furman found that the readings of the oxygen-normal calomel electrode cell were much more nearly constant in acid than in alkaline solutions. During the first hour before or after titrations there was a drift of from 5 to 10 mili. v. (in one case 15) in acid solution, and one of 30 to 60 mili. v. in alkaline media.

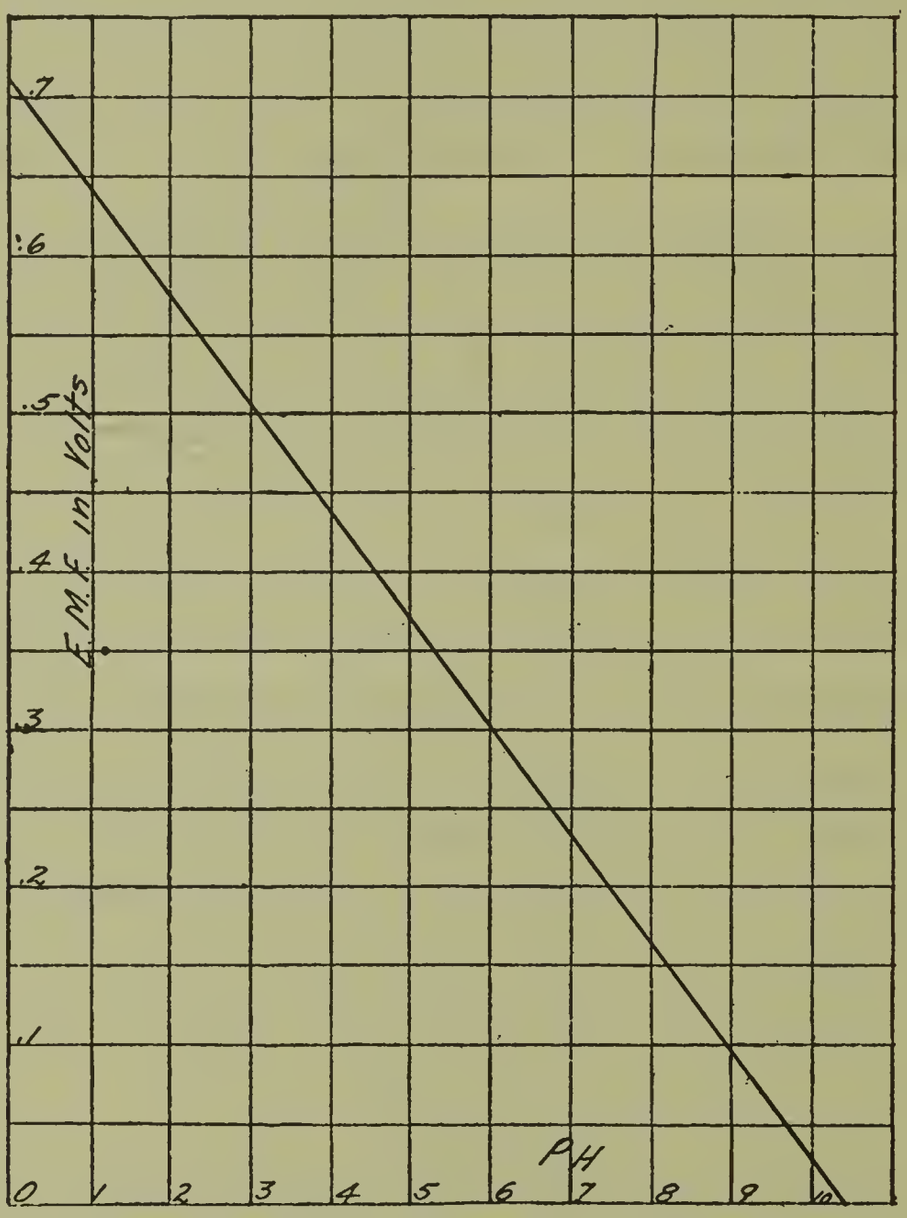

FIG. 1. Calibration Curve. Oxygen Electrode-Normal Calomel vs. pH.

Usually after 15 to 20 min. the readings were steady enough to allow ordinary analytical determinations to be made. If the electrode was saturated with oxygen the titration could be commenced immediately. During the titrations the readings were almost as steady as those during ordinary hydrogen electrode titrations.

Knowing from Furman's work that there was a drift in the

electromotive force readings of the oxygen electrode, but that the variation became quite small (only 1 or 2 mili. v.) after 15 to 20 min., a calibration chart was determined on that basis, using buffer mixtures as described by Clark[9]. For values in the vicinity of the neutral point, Palitzsch's borax-boric acid mixture was used; for those values of pH from 3.6 to 5.6 Walpole's acetate mixtures were made. In this manner the buffer mixture was checked against the hydrogen electrode and then used to determine the value for the corresponding oxygen electrode reading, against the normal calomel electrode. A graph was then plotted between pH and the e. m. f. readings. (See Fig. 1). As a variation of 6 mili. v. would cause a change of 0.1 pH, a drift of 2 or 3 mili. v. would cause a change of only 0.05 pH.

EXPERIMENTS ON PLATING.

Knowing that M. R. Thompson[4] had conducted careful experiments on nickel plating, in which the acidity was controlled by the colorimetric method, it was decided to see if the oxygen electrode would give similar results. Accordingly, a solution was used containing the following proportions of materials:

Nickel sulfate	140 g./L.
Boric acid	16 g./L.
Sodium fluoride	4 g./L.

A titration curve was developed by adding 0.2 *N* acid or 0.2 *N* alkali solution to 50 cc. of a sample of the plating bath, observing the pH at each step and plotting the results. Curve A, Fig. 2, shows the result obtained.

Under similar conditions a cobalt plating bath of the following composition was used to determine its titration curve.

Cobalt sulfate	312 g./L.
Sodium fluoride	14.2 g./L.
Boric acid	nearly to saturation.

The result is shown in curve B of Fig. 2.

These curves are analogous to those of Thompson, and show the buffer action of the sodium fluoride and boric acid in each case.

[9] The Determination of Hydrogen Ions, W. M. Clark, 1920 Edition.

NICKEL PLATING.

Deposition was conducted under the following conditions, using the solution mentioned above. The plating was carried out at approximately 22° C. without stirring. Deposits were made upon copper plates, smooth but not polished. The anodes were electrolytic nickel, two in number, with the cathode between. The

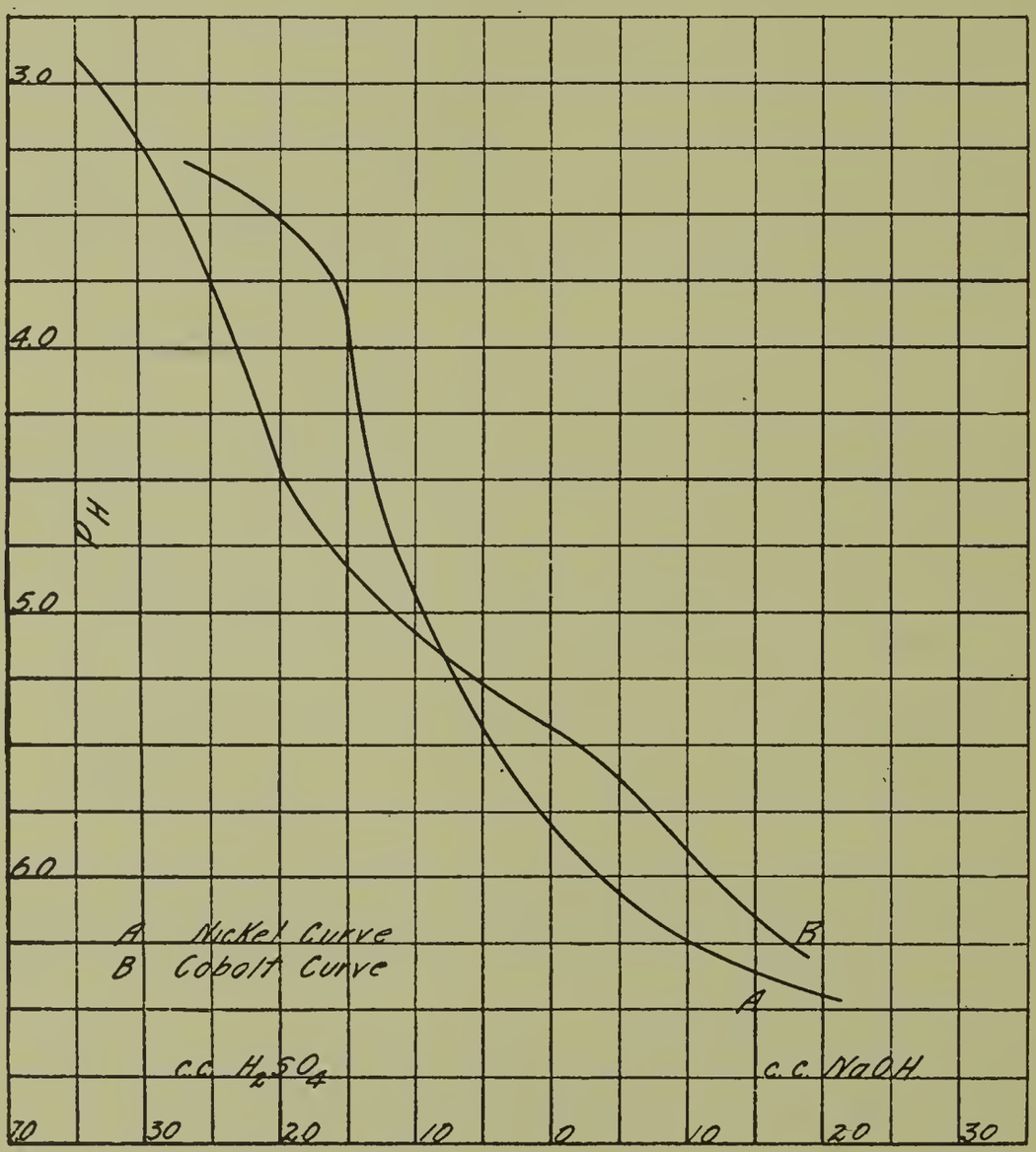

FIG. 2. Titration curves obtained by using 0.2 *N* H_2SO_4 and 0.2 *N* NaOH.

relation between anode and cathode area was varied to obtain, as far as possible, equal anode and cathode efficiencies. The pH of the bath was adjusted by adding sulfuric acid or sodium hydroxide, and was measured by the oxygen electrode. The cathode current efficiencies were measured by a copper coulometer. The current density was 1.5 amp. per sq. dm. A curve (Fig. 3) was plotted between the current efficiency and the corresponding pH

value. These results are similar to those of Mr. Thompson, though somewhat lower in efficiency for the same pH values.

Character of deposits:

At pH 6 the deposit was greyish white and very dense, adherent and smooth with no gas streaks or pits.

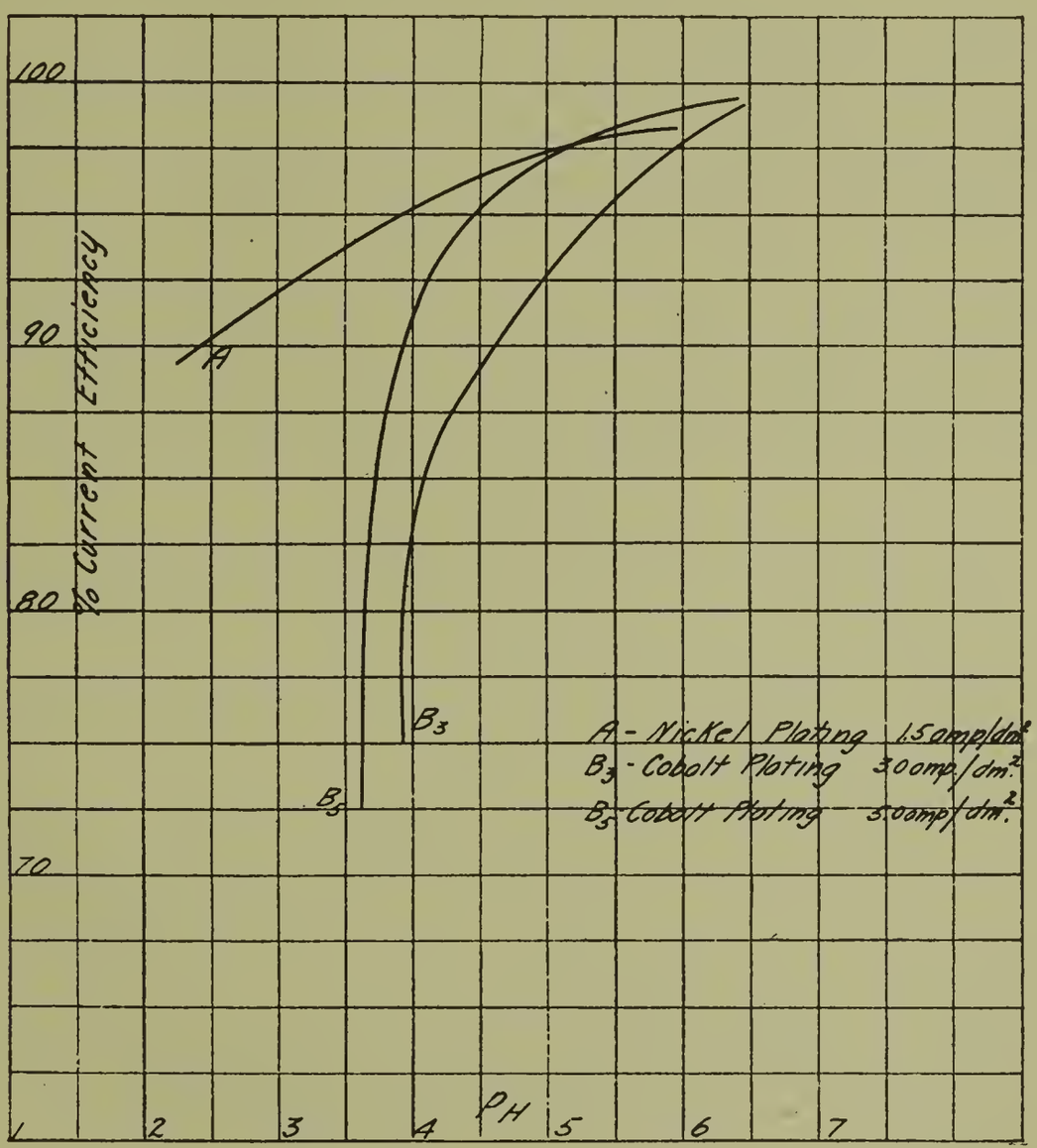

FIG. 3. Current Efficiency vs. pH.

At pH 4.5 fairly good deposits were made, but a few gas streaks were noticed.

Below pH 3.5 the deposits tended to peel at the edge, and gas streaks were more pronounced.

COBALT PLATING.

Cobalt was deposited under conditions similar to those for nickel. The bath used was similar to one recommended by H. T.

Kalmus[3], except that sodium fluoride was substituted for sodium chloride because it would improve buffer action. The composition of the bath is given previously, and designated bath C. The same apparatus was used and similar readings were taken on cobalt plating, runs being made at 3 and also 5 amp. per sq. dm. Curves were plotted showing the relation between pH and current efficiency. (See Fig. 3).

The cobalt deposits at about pH 6 were dense and adherent, taking a good polish. Gas streaks were absent. The acidity of the bath tended to remain constant. At the higher current density the plates tended to curl at the edges.

Below pH 4.5 poor plates resulted and the acidity of the bath changed, tending toward a higher pH or condition of less acidity. The current efficiency below pH 4.5 falls quite rapidly, more rapidly than in the nickel bath for the same region of acidity.

SUMMARY.

1. The hydrogen electrode can not be used for obtaining the pH of solutions of metals which for any reason fall below hydrogen in the electromotive series.

2. The oxygen electrode can be used to control the acidity of both nickel and cobalt plating baths.

3. It is known that the oxygen electrode is subject to drift in e. m. f. readings, but with reasonable care an accuracy of about 0.1 pH can be expected in determining the pH of plating baths. This statement may be modified as the result of further experiments under varying conditions.

4. The best deposits of both nickel and cobalt and the highest current efficiencies at the cathode were obtained at a pH value of about 6.

5. The cathode current efficiencies for different current densities are about the same at pH 6.

6. Further work is needed to establish the range of accuracy and applicability of the oxygen electrode in determining pH under varying conditions of plating.

DISCUSSION.

O. W. Storey[10] (*Communicated*): The results of Montillon and Cassel clearly point out the difficulties in obtaining consistent

[10] C. F. Burgess Labs., Madison, Wis.

results when determining the pH of nickel plating solutions. The use of this method in the nickel plating room is limited to those establishments that have the technical skill available to determine the pH value correctly. For the many nickel platers who are not technically trained, or who do not have such technical assistance, a much simpler method is desirable.

It was my privilege to devise such a simple method about five years ago. This simple method uses the principles of pH control by observing the colors obtained when a methyl red solution is added to a nickel plating solution. The details of this method were given in a paper before the 1921 meeting of the Electroplaters' Society.[11]

I found that a *methyl red* solution when added to a nickel plating solution in correct proportions, gave a wide variation in color, depending upon the acidity or alkalinity of the plating solution. The color varies from a light green or yellow green when alkaline, which becomes yellow, orange brown, brownish purple and purple as the nickel solution increases in acidity. By comparing the color to a standard which is made from the nickel solution when giving the best plating results, and which usually results in a yellow solution, it is easy to control the nickel solution to close limits with a bottle of methyl red solution and a few test tubes. In other words, a yellow solution resulting from the addition to methyl red to the nickel plating solution indicates the correct pH of about 6.

The commercial utility of this method is demonstrated by its widespread use. It has been used in one plant for five years, and it permitted a man of little experience to keep perfect control over his nickel plating solutions.

Whether this method may be used for controlling cobalt baths is a matter of experiment. If methyl red does not give the desired color indication, some other indicator can possibly be found. It would be of much interest and value to practical platers if Montillon and Cassel could carry on these color tests in connection with their work on the pH of the nickel and cobalt plating solutions.

VICTOR K. LAMER[12] (*Communicated*) : The interesting paper of

[11] This paper is discussed by Haas, *Metal Industry*, **21**, 273 (1923).

[12] Assistant Professor, Dept. of Chemistry, Columbia University.

Montillon and Cassel emphasizes the need of methods for the determination of pH in solutions containing salts of metals more noble than hydrogen. The oxygen and manganese oxide electrodes to be sure do enable us to obtain approximate measures of the pH in the presence of strong oxidizing agents, but the results thus far obtained have not shown as high a degree of precision and reproducibility under different conditions as is often desired. Until we reach a more complete understanding of the conditions necessary for the strict reversibility of these electrodes, the results obtained with them must be considered as provisional.

In connection with some studies having as their object the relation between pH and the adsorption of the more noble metallic ions, Paul M. Horton and the writer have found that results equal in reproducibility and accuracy (0.0002 v.) to the hydrogen electrode can be obtained in the presence of copper salts as concentrated as saturated copper sulfate by the use of the *benzoquinhydrone electrode*. Details on the use and reliability of this electrode for titration work as well as its freedom from the effects of atmospheric oxidation have been published.[13]

The simplicity of the technique, which requires only the addition of a few crystals of quinhydrone to the solution in place of gaseous hydrogen, and the accuracy and rapidity with which measurements can be made, highly recommend the method in those cases where the oxidation potential of the original solution is not greater than (0.6990 — 0.059 pH) v. This comprises acid solutions of the ions of all metals in the state of highest valence up to and including copper in the e. m. f. series, as well as weak oxidizing anions like ferrocyanide.

With this method we have been able to measure the hydrolysis-concentration curve of copper sulfate, and have determined the quantitative effects of the presence of free acid on the adsorption of copper ions by charcoals of alkaline manufacture. A marked reduction in adsorption occurs at acidities less than pH 4.

The reproducibility and stability of the potentials obtained with pure nickel sulfate solutions, to which varying quantities of copper sulfate were added, lead us to infer that the method ought to be of practical value for commercial plating baths, or in cases

[13] LaMer and Parsons; Proc. Soc. Exp. Biol. and Med., **20**, 239 (Feb., 1923); J. Biol. Chem., **57**, 613 (1923), and LaMer and Rideal, J. A. C. S., **46**, 223 (1924).

where the hydrogen electrode technique fails owing to the "poisoning" effects of copper ions.

C. P. MADSEN[14]: The degree of accuracy of pH control requiring electrometric methods is made necessary in nickel and cobalt solutions only by the presence of iron. It is, however, highly desirable to be able to check colorimetric readings by electrometric methods, and the hydrogen electrode is inherently inapplicable to solutions containing sulfates because of the formation of peroxides or persulfates during electrolysis. I therefore think that the oxygen electrode is an important contribution to the art, as a means for checking colorimetric pH readings in solutions containing sulfates.

EDWIN SMITH, JR.[15]: Like Mr. Madsen, we find we can use a wide range of acidity in our nickel plating solutions without detrimental results, providing we have no *organic matter* present.

W. BLUM[16]: I would call the attention of the two previous speakers to the fact that they were both doing work at very high current densities, at which, as all of these curves show, the cathode efficiencies are practically independent of the pH. In other words, the pH becomes more important the lower the current density that is used.

EDWIN SMITH, JR.: We find that that is true. In our still cells we have to watch the pH more carefully than we do in the cells with rotating cathodes.

M. R. THOMPSON[17] (*Communicated*): The authors have applied another instrument to the study of plating solutions, and deserve the congratulations of all the investigators in this field for their very interesting contribution.

One factor in the hydrogen-ion concentration of nickel solutions is the fact that even supposedly quite pure samples of salts may contain a little free acid. It is important to keep in mind that a solution prepared from such a salt will not exhibit a definite hydrogen-ion concentration, unless it has been treated with nickel hydroxide or carbonate, that is, "neutralized."

[14] Consulting Engr., New York City.
[15] Chief Chemist, Edison Storage Battery Co., Orange, N. J.
[16] Chemist, Bureau of Standards, Washington, D. C.
[17] Chemist, Bureau of Standards, Washington, D. C.

The results of this paper show, in effect, that indicators in nickel solutions actually do give hydrogen-ion values close to the true hydrogen-ion scale. Previously, this was assumed on general grounds, but not definitely proven. The values used in the past, even if they might have been arbitrary, were, however, just as useful for solution control purposes. It is now established by the oxygen electrode that indicators give accurate as well as reproducible results in nickel solutions.

On account of the greater cost and complexity, it is difficult to see how the electrode method can displace indicators for plant control purposes, except in unusual cases where, *e. g.,* oxidizing substances are present which interfere with indicators, or else an unusual amount of turbidity is encountered and for some reason filtration of samples is not desired. For supplementary purposes in research the electrode may at times prove useful. It is to be hoped that the authors will subsequently furnish details of the recommended type of oxygen electrode vessel.

G. H. Montillon[18] (*Communicated*): The writer agrees with O. W. Storey regarding the simple method of control of acidity of nickel plating solutions, using methyl red indicator for the range pH 5.0 to 6.0. However, our work has given:

1. A plausible explanation of the reason for the failure of the hydrogen electrode in certain solutions.

2. A means of checking the pH value of nickel and cobalt plating baths as determined in other ways.

Further, it is hoped that this method can be extended to other fields, in which it may be impractical to use either the hydrogen electrode or the colorimetric method. Work in this laboratory on the use of the Bailey electrode has shown a great saving of time in making determinations with the oxygen electrode, and we have found that consistent checks are obtained in comparing the oxygen electrode method with the colorimetric.

Mr. M. R. Thompson has kindly called my attention to the fact that his curve D[19] is not strictly comparable with ours as the boric acid concentration in the plating solution was 0.5 *M* for his curve and only 0.25 *M* for ours. The curves are analogous, however.

[18] University of Minnesota.
[19] Trans. Am. Electrochem. Soc., **41**, 344 (1922).

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

CORROSION RESISTANCE OF STEEL ELECTROPLATED WITH ZINC AND WITH ZINC-MERCURY ALLOYS.[1]

By C. J. Wernlund.[2]

Abstract.

Corrosion studies of three types of zinc electrodeposits were made. Deposits containing 2 per cent of mercury were more resistant than deposits of pure zinc obtained from either sulfate or standard cyanide baths.

There was recently described[3] a process for producing an electrodeposit of zinc-mercury alloy. Such a deposit has been found to be more resistant to atmospheric corrosion than pure zinc deposits obtained from sulfate baths, and also from standard cyanide baths. This paper reports a study of the relative rates of corrosion of different kinds of zinc electrodeposits on mild steel. The study was made over a period of about two years, during which time many specimen deposits were made and subjected to corrosion tests. Atmospheric corrosion tests were made, but because of lack of time some of them are not yet completed. Because of the long time required for the completion of such tests, samples of each type of deposit were also subjected to the salt spray corrosion test proposed by the Bureau of Standards.[4] This test is made by exposing the plated samples to a continuous spray of 20 per cent sodium chloride solution. The spray is produced by means of compressed air.

[1] Manuscript received February 15, 1924.

[2] Research Department, The Roessler and Hasslacher Chemical Company, Perth Amboy, N. J.

[3] Jos. Haas, Jr., U. S. Patent 1,451,543; Proctor and Wernlund, U. S. Patent 1,435,875.

[4] Bureau of Standards, Circular No. 80, "Protective Metal Coatings for the Rust Proofing of Iron and Steel."

DETAILS OF THE TESTS.

Preparation of Test Samples. All the test samples used in these corrosion tests were cleaned as follows:

1. Hot caustic soda pickle to remove all grease.
2. Water rinse.
3. Hot 10 per cent sulfuric acid pickle to remove all scale and rust.
4. Water rinse.
5. Ten-second bright dip in the following solution: Nitric acid, C. P., 25 per cent; sulfuric acid, C. P., 50 per cent; water, 25 per cent, all by volume. Always use iron wire hooks in this dip.
6. Water rinse.
7. Five-minute immersion in hot caustic soda solution.
8. Hot water rinse.
9. Dried, weighed and plated.

Purity of Materials. Since all the plating solutions were prepared from the purest obtainable chemicals, as specified below, the amount of undesirable impurities, often introduced from these sources, was negligible. The impurities in the anodes used were less than 0.05 per cent Pb; 0.03 per cent Fe; 0.03 per cent Cd.

Electrodes Used. All electrodes measured 6 in. x 3 in. x 1 in. (152 mm. x 76 mm. x 25 mm.) For the zinc sulfate cell and the old type zinc cyanide cell anodes of electrolytic zinc were used. For the improved cyanide process the anodes were an alloy of electrolytic zinc and distilled mercury, containing 2 per cent of the latter.

Plating Solutions Used. The sulfate bath contained 240 g./L. (32 oz./gal.) zinc sulfate, C. P.; 30 g./L. (4 oz./gal.) magnesium sulfate, C. P.; and 0.75 g./L. (0.1 oz./gal.) sulfuric acid, C. P.

The two cyanide baths each contained 37.5 g./L. (5 oz./gal.) zinc cyanide (55 per cent Zn); 22.5 g./L. (3 oz./gal.) sodium cyanide, 96 to 98 per cent; and 30 g./L. (4 oz./gal.) sodium hydroxide, C. P.

Operating Data. The solution for the improved process was electrolyzed for two hours, using zinc-mercury alloy anodes and a sheet-metal cathode, before being used for plating the test pieces.

Operating Data for Preparation of Test Sheets.

	Sulfate Process	Old Type Cyanide	Improved Cyanide
Volume of plating solution.	12 L.	12 L.	12 L.
Distance between electrodes.	6.4 cm. (2.5 in.)	6.4 cm. (2.5 in.)	6.4 cm. (2.5 in.)
Anode area	7.80 to 13.80 sq. dm. 0.84 to 1.48 sq. ft.	5.20 to 6.90 sq. dm. 0.56 to 0.74 sq. ft.	5.20 to 6.90 sq. dm. 0.56 to 0.74 sq. ft.
Anode current density.....	0.55 to 1.10 amp./sq. dm. 5.00 to 10.00 amp./sq. ft.	1.00 to 2.00 amp./sq. dm. 9.30 to 18.60 amp./sq. ft.	1.30 to 1.60 amp./sq. dm. 12.00 to 15.00 amp./sq. ft.
Cathode area	2.60 to 3.40 sq. dm. 0.28 to 0.37 sq. ft.	2.60 to 3.40 sq. dm. 0.28 to 0.37 sq. ft.	2.60 to 3.40 sq. dm. 0.28 to 0.37 sq. ft.
Cathode current density...	1.60 to 2.10 amp./sq. dm. 15.00 to 20.00 amp./sq. ft.	2.10 to 2.70 amp./sq. dm. 20.00 to 25.00 amp./sq. ft.	2.70 to 3.20 amp./sq. dm. 25.00 to 30.00 amp./sq. ft.
Temperature	20 to 25° C. 68 to 77° F.	38 to 40° C. 100 to 104° F.	38 to 40° C. 100 to 104° F.
E. M. F.	3.4 to 3.7 v.	4 to 5 v.	4 to 5 v.
Zn deposited per amp. hr..	.....	.....	1.1 to 1.2 g.

DISCUSSION OF THE IMPROVED CYANIDE PROCESS.

The chief distinguishing feature of this process consists in the use of zinc-mercury anodes. Other variations from present cyanide plating practice are:

1. A smaller anode surface is used and a bus bar e. m. f. of from 4 to 5 volts is maintained.

2. Solutions of somewhat lower cyanide and zinc concentrations are used to advantage, thus minimizing "hydrolysis" and "dragout" losses.

3. A materially higher cathode current density is used.

The mercury is added to the anode primarily to obtain a zinc-mercury alloy deposit. The per cent of mercury in the anode determines the per cent of mercury in the bath and in the deposit. Without the applied e. m. f. the alloy anodes are practically insoluble in the plating solution, and as a result the anode and cathode current efficiencies are equalized to within about 2 per cent. The solution is thus stabilized, replenishing of cyanide occurs less frequently, and the constant chemical supervision which the old process required is no longer necessary.

Over a year of successful commercial operation of zinc cyanide solutions with these alloy anodes has demonstrated that very smooth, light, silvery colored deposits can be consistently produced. These coatings are remarkably free from porosity, are less reactive chemically than other zinc deposits, and do not stain or discolor appreciably during exposure.

It should also be pointed out that when too much mercury is added to the zinc bath in the form of mercury salts, deposits may easily be obtained containing up to 30 per cent or more of mercury. Since zinc-mercury coatings containing over 3 per cent of mercury crack upon bending the base metal sharply, and metallic mercury has been found to sweat out of heavy deposits, containing approximately 8 per cent of mercury, upon aging, the careful adjustment of the mercury content of the solutions is essential.

CORROSION TEST DATA.

The corrosion test data are given below in Tables I and II. The evaluation of the protection of steel or iron against rust,

afforded by electro zinc deposits, has been accomplished by two methods, namely, (a) salt spray tests, and (b) atmospheric corrosion tests.

The salt spray test was carried out exactly as outlined by the Bureau of Standards.[5] The inside dimensions of the stoneware tank used were 30 x 15 x 9 in. (76.2 x 38.1 x 22.9 cm.) The spray was run with filtered air at 500 g. per sq. cm. (7 lb. per

TABLE I.

Results of Salt Spray Tests.

Blue annealed iron sheets, 12-mesh wire screen and 6-inch clincher rim sections, plated in a sulfate zinc bath, a cyanide zinc bath, or a cyanide zinc-mercury bath.

Base Metal	Kind of Bath	Weight of Coating		Number of Samples	Average Time for Appearance of Rust Hours	Calculated Time Appearance of Rust for 0.10 oz. Zn/sq. ft. Hours
		mg./sq. dm.	oz./sq. ft.			
Steel sheets	Sulfate	156	0.051	6	15	29
Steel sheets	Cyanide	162	0.053	6	34	64
Steel sheets	Zn-Hg Cyanide	171	0.056	6	45	80
Wire screen	Sulfate	122	0.040	6	7.5	19
Wire screen	Cyanide	165	0.054	6	23	43
Wire screen	Zn-Hg Cyanide	281	0.092	6	47	51
Rim sections	Sulfate	347	0.114	6	18	16
Rim sections	Cyanide	275	0.090	6	57	63
Rim sections	Zn-Hg Cyanide	253	0.083	3	61	74

sq. in.) pressure. The temperature at which the tests were run varied from 17 to 25° C. The salt spray test was chosen because it is widely recognized as the best accelerated corrosion test for galvanized iron. The atmospheric corrosion test was chosen to check the results of the salt spray test, and to give actual service test data as to the actual value of the three kinds of zinc coatings. The atmospheric corrosion tests were conducted at Perth Amboy, N. J., on the roof of a two-story building. They were begun in December, 1923. The samples were suspended from wooden racks by heavily zinc-plated steel wire.

Repeated observations of the atmospheric corrosion test sam-

[5] *Loc. cit.*

ples have shown that the rate of atmospheric corrosion of these coatings depends chiefly, if indeed not entirely, upon the number of hours the coatings are kept wet by rainy weather. The actual rusting of the test samples occurred during rainy weather. During dry weather no rusting was observed.

TABLE II.

Results of Atmospheric Corrosion Tests.

Blue annealed iron sheets, 12-mesh wire screen and 6-inch clincher rim sections, plated in a sulfate zinc bath, a cyanide zinc bath, or a cyanide zinc-mercury bath.

Base Metal	Kind of Bath	Weight of Coating		Number of Samples	Average Time for Appearance of Rust	Calculated Time Appearance of Rust for 0.10 oz. Zn/sq. ft.
		mg./sq. dm.	oz./sq. ft.		Days	Days
Steel sheets	Sulfate	248	0.081	6	85	105
Steel sheets	Cyanide	257	0.084	3	127	151
Steel sheets	Cyanide	272	0.089	3	>133	...
Steel sheets	Zn-Hg Cyanide	272	0 089	6	>133	...
Wire screen	Sulfate	338	0.111	6	28	25
Wire screen	Cyanide	354	0.116	6	58	50
Wire screen	Zn-Hg Cyanide	462	0.151	6	96	63.5
Rim sections	Sulfate	609	0.200	6	29	14.5
Rim sections	Cyanide	257	0.084	6	121	144
Rim sections	Zn-Hg Cyanide	213	0.070	2	125	178
Rim sections	Zn-Hg Cyanide	243	0.080	3	>133	...

NOTE: In the tests recorded in Tables I and II an effort was made to work with zinc deposits of approximately 15. g./sq. m. (0.05 oz./sq. ft.) for the salt spray tests, and 30 g./sq. m. (0.10 oz./sq. ft.) for atmospheric corrosion tests (the sulfate rim sections of Table II excepted). The variations of the weights of the coatings may have influenced the comparisons slightly.

All the test samples were prepared and tested under as nearly identical experimental conditions as possible. The salt spray test data have been substantiated by the atmospheric corrosion data in so far as the latter has been completed.

SUMMARY AND CONCLUSIONS.

1. The relative values of the different types of deposits as indicated by the salt spray and by atmospheric corrosion tests may be recorded as follows:

Type of Bath	*Salt Spray Tests*			*Atmospheric Corrosion Tests*		
	Steel Sheets	Wire Screens	Rim Sections	Steel Sheets	Wire Screens	Rim Sections
Zn-Hg cyanide.	100	100	100	Data in-	100	100
Cyanide.....	80	84.3	85.2	complete	78.8	81
Sulfate.....	36.3	37.3	21.6		39.4	8.2

2. Salt spray tests give fairly reliable estimates of the resistance of zinc deposits to atmospheric corrosion.

3. One pound of zinc-mercury alloy deposited from the improved cyanide solution furnishes as much protection against corrosion as 1.25 lb. deposited from the ordinary cyanide solution, or from 2 to 4 lb. deposited from the sulfate solution.

4. These corrosion tests show the superiority of cyanide zinc deposits over sulfate zinc deposits, and most strikingly in the case of deeply recessed steel parts.

DISCUSSION.

M. R. THOMPSON[6]: I would like to ask Mr. Wernlund whether the 100's, top of page 279, are all the same?

C. J. WERNLUND: We have let the figure "100" represent the most resistant coating in each set of samples. The remaining figures at the top of page 279 are then calculated from Tables I and II.

G. B. HOGABOOM[7]: Mr. Wernlund, how did you keep 0.1 oz./gal. (0.75 g./L.) sulfuric acid in a zinc sulfate solution?

C. J. WERNLUND: The acidity was corrected daily, and did not fall below 0.38 g./L. (0.05 oz./gal.) of sulfuric acid. It is better to add the mercury to the solution by means of the anode. Due to the fact that mercury plates out readily from cyanide solutions, an extremely small concentration of metal must be maintained. If the mercury is added in the form of salts, it is necessary to

[6] Chemist, Bureau of Standards, Washington, D. C.
[7] Research Plater, P. and F. Corbin, New Britain, Conn.

make small additions to the bath very frequently, in order to obtain a fairly constant composition in the coating. By using the zinc-mercury alloy anode, the mercury content regulates itself in the bath automatically, and the composition of the anode closely reflects the composition of the mercury content in the deposit itself. In the casting of anodes containing mercury there is only a very small loss of metal.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

AN INTERMITTENT IMMERSION TEST AS AN AID IN EVALUATING ZINC COATS PLATED ON IRON AND STEEL.[1]

By F. F. Farnsworth and C. D. Hocker.[2]

Abstract.

A test for evaluating the quality of an electrodeposit of zinc on iron and steel is described; it consists of a series of immersions of the samples in a solution of ammonium chloride, alternating with periods of drying in the air. The test shows up discontinuities and thin spots in zinc coatings in a discriminating manner; it differentiates zinc coatings plated from a sulfate and from a cyanide bath; and it may be used to compare the effectiveness of different methods of precleaning the iron and steel before plating.

Accelerated tests to judge the protection against corrosion afforded to iron by a plated finish, are open to the objection that such tests may not be a reliable measure of what happens to the material under conditions of service. In selecting or developing such a test, therefore, one must be guided largely by what methods appear reasonable, and are found to disclose best the differences in samples known to differ in quality. This paper describes an accelerated test for the quality of zinc electrodeposited on iron, and discusses the evidence we have that the test is reasonable and discriminating.

The test proposed is one in which plated specimens are submitted to cycles of immersion in an ammonium chloride solution and drying in air until the appearance of rust.

A test for the quality of electroplated zinc on iron should have the following characteristics:

[1] Manuscript received February 20, 1924.

[2] Research Laboratories of the American Telephone and Telegraph Co. and the Western Electric Co., New York City.

1. It should detect weak spots that exist in the coating, such as pin-holes or thin spots, and should yield a clear indication of these weak spots.

2. It should be capable of completion in a few hours or at most in a few days.

The method probably best known for judging the quality of zinc plated iron is the salt spray test. In our effort to apply this test we have found it to be not selective in picking weak spots, which we knew to exist in coatings, and somewhat erratic in differentiating between coatings, unless they are distinctly different in quality. Some evidence concerning this is presented later.

Another method sometimes used to judge the quality of electroplated zinc coats is that in which the samples are immersed in distilled water through which air is continuously bubbled; but this test is undesirably slow in detecting weaknesses other than those which are marked. With heavily plated coatings, say half of a thousandth of an inch in thickness, weeks or even months may be required before the first appearance of rust.

Zinc is usually more susceptible than iron to attack by solutions. Accordingly it does not appear promising to attempt to develop a method of locating pin-holes in a zinc plate on iron by a test similar to that used for nickel plated or tin plated iron, namely, immersing the sample in a 10 per cent gelatin solution containing acidified ferrocyanide which acts preferentially on the exposed iron.

Zinc is distinctly electronegative to iron. Consequently, if a zinc-iron couple is immersed in a solution of an electrolyte, the tendency is for zinc to dissolve and for the iron to remain as metal. Thus, if a pin-hole occurs in a zinc plate on iron, the zinc protects the exposed iron from rusting, unless the pin-hole is of considerable size. Hence it seems reasonable to expect that in any test to evaluate zinc coats on iron, the pin-holes or small exposed areas will tend to remain free from rust so long as the surface of the plated specimen remains wet with a conducting solution, a condition which obtains in the cases of a continuous immersion or spray with an electrolyte. We have observed that pin-holes or small exposed areas tend to remain free from rust when zinc plated samples have been continuously immersed in a variety of solutions, such as dilute solutions of sodium chloride, ammonium chloride, potas-

sium iodide, aluminum sulfate, magnesium chloride, potassium persulfate, and bromine water. In no case did vigorous aeration of these solutions cause a satisfactory appearance of red rust to mark the location of the pin-holes or small exposed areas of iron; even the oxidizing solutions, potassium persulfate and bromine water were not different in this respect from the others.

However, it was observed that exposed areas of iron, which did not show red rust when the plated specimens were continuously immersed in the above solutions, did become rusted when the specimens were lifted out of the solution and allowed to dry in the air. This observation led us to the viewpoint that an intermittent immersion test, in which the samples were allowed to dry between immersions, might be reasonably satisfactory.

In observing the deportment of zinc-plated iron, continuously immersed in solutions containing both ammonium chloride and ammonium carbonate, we noted that white incrustations of zinc carbonate formed in spots on the plate.. These could be induced to form at points where pin-holes were intentionally made, and also at points of contact with foreign materials such as a fragment of glass, a thread, a pencil mark, or mark made on the zinc plate with a piece of metallic tin or lead. These white spots were also induced at points where particles of the corrosion products were placed, and there was a marked tendency for the progress and distribution of corroded areas on the specimens to follow the chance distribution of corrosion products which became dislodged and settled elsewhere on the plates. This observation accords with the work of Bengough and Hudson[3], who found that if corrosion were caused to start at a central point of a zinc plate slowly rotated in a horizontal plane in a corroding medium, the corrosion products radiate spirally outward toward the edges of the plate. These observations led us to the belief that a method of removing the corrosion products as they are formed would be desirable.

As a means of keeping the corrosion products removed, it was considered promising to try solutions of ammonium salts which do not form insoluble compounds with zinc solutions, as ammonium carbonate does. Some preliminary experiments showed that ammonium chloride solutions did keep the zinc surface clean,

[3] Results achieved by the Corrosion Committee British Institute of Metals, Chem. and Met. Eng., 26, 301 (1922).

either when the samples were continuously or intermittently immersed in the solution; and aerating the solution or allowing it to stand without aeration did not affect this.

It was our conception that the reagent used to keep the corrosion products removed from the zinc surface should have no action, or only a slow action on the uncorroded zinc. To determine if this were characteristic of the action of ammonium chloride solutions, some studies were made of the rate of attack on zinc by these solutions, both when aerated to promote the formation of corrosion products and when air was excluded. Table I records some observations on (1) the rate of attack on zinc and iron by aerated ammonium chloride solutions of various strengths; (2) the comparative effect of aeration and exclusion of air on the rate of attack of zinc by ammonium chloride solutions; and (3) the effect of certain oxidizing agents in accelerating the rate of attack on zinc and iron by ammonium chloride solutions.

The aeration of solutions was accomplished by an arrangement similar to that recently described by Thompson and McKay[4]; it consists essentially in supplying air to the solution through the pores of an alundum crucible, and gathering the ascending bubbles by an inverted funnel which delivers them near the top of the solution but prevents them from coming in contact with the suspended metal samples. The volume of the aerated solution used in these experiments was about 10 L., and the total area of the suspended samples, approximately 2.3 sq. dm.

In the experiments in which air was excluded (Series II) an apparatus was used which enabled us to immerse the test sample in a solution which had been boiled, cooled in a stream of purified nitrogen and sealed when room temperature had been reached. The volume of the solution used in these experiments was 100 cc., and the surface area of the immersed sample, 0.4 sq. dm. The samples were left sealed in the solution for the periods of time recorded in the table before the seal was broken to remove the samples for weighing.

The samples of iron used were cleaned cold-rolled mild steel plates; the zinc samples were sheet zinc electroplated with zinc from a cyanide solution.

[4] Thompson and McKay, Jour. Ind. and Eng. Chem., 15, 1114, (1923).

The loss in weight of the samples in mg./sq. dm./hr. was taken as a measure of the extent of attack. In the cases of the zinc samples the ammonium chloride kept the surfaces entirely free of any visible corrosion products, and a few analyses showed that the loss in weight of the sample checked fairly closely with the zinc gained by the solution. In the cases of the iron samples, the corrosion products left on the surfaces were so loosely adhering that the plates could easily be wiped clean. To prepare the samples for weighing, they were thoroughly washed in water, dipped in alcohol, quickly dried, and finally rubbed with cotton.

The following points may be noted from Table I:

1. The rate of attack of both zinc and iron in aerated solutions is not much affected by change in concentration of ammonium chloride over a range of 0.09 M to 1.8 M (0.5 to 10 per cent.) These experiments were carried out using a relatively large volume of solution and samples having a small surface area, conditions similar to those employed when the proposed intermittent immersion test is used to evaluate zinc plated samples.

As a point of comparison, an experiment, not listed in Table I, made with three samples of zinc continuously immersed in an aerated solution of sodium chloride for 33.5 hr. at 22 ± 1° C., showed the rate of attack to be 1.70 mg./sq. dm./hr., which is about one-third as rapid as that shown by aerated ammonium chloride solution of the same strength.

2. The rate of attack of zinc in air-free solution of ammonium chloride is affected by the concentration of the solution, and also by the length of time of the test, the most rapid attack occurring in the experiment using the strongest solution left sealed for the shortest time. In these experiments the volume of solution was 100 cc., and total surface of immersed sample, 0.4 sq. dm.

3. The rate of attack of the zinc by the solutions containing small amounts of oxidizing agents is several times more rapid than that of the solutions merely aerated; and the latter act several times faster than the solutions from which air is excluded. This indicates that the action of the ammonium chloride is to attack the zinc corrosion products rather than the metal, since under all three conditions of experiment the zinc specimens and the solution remain free of undissolved corrosion products.

TABLE I.

Rate of Attack of Iron and Zinc by Ammonium Chloride Solutions.

Series of Tests Illustrating	Metal	Corroding Medium	Number of Samples	Aeration	Time of Test in Hours	Temp. in °C.	Loss of Weight of Sample in mg./sq. dm./hr.
I. Rate of attack of iron and zinc by aerated NH_4Cl solutions of different strengths.	Fe	0.090 M (0.5%) NH_4Cl	10	Yes	52	18 ± 1	2.15
		0.370 M (2%) NH_4Cl	12	Yes	65	18 ± 1	2.06
		1.800 M (10%) NH_4Cl	5	Yes	61.5	18 ± 1	2.12
	Zn	0.090 M NH_4Cl	3	Yes	38	22 ± 1	5.53
		0.370 M NH_4Cl	3	Yes	60	22 ± 1	4.44
		1.800 M NH_4Cl	3	Yes	65	22 ± 1	4.43
II. Effect of exclusion of air on rate of attack of zinc by NH_4Cl solutions.	Zn	0.108 M NH_4Cl	1	No	21	25 ± 1	0.163
		0.108 M NH_4Cl	1	No	120	25 ± 1	0.066
		1.000 M NH_4Cl	1	No	21	25 ± 1	0.455
		1.000 M NH_4Cl	1	No	120	25 ± 1	0.194
		0.370 M (2%) NH_4Cl*	2	No	1	100	1.35
III. Rate of attack of zinc and iron by NH_4Cl solutions containing certain oxidizing agents.	Fe	0.370 M NH_4Cl + 0.1% H_2O_2	3	Yes	18	22 ± 1	19.1
		0.500 M NH_4Cl + 0.01M $(NH_4)_2S_2O_8$	3	Yes	19	20 ± 1	27.4
	Zn	0.090 M NH_4Cl + 0.03% H_2O_2	6	Yes	17	21.5 ± 1	7.5
		0.090 M NH_4Cl + 0.10% H_2O_2	3	Yes	17	22 ± 1	16.34
		0.370 M NH_4Cl + 0.03% H_2O_2	6	Yes	17	21.5 ± 1	14.3
		1.800 M NH_4Cl + 0.03% H_2O_2	3	Yes	18	21 ± 1	28.23
		1.800 M NH_4Cl + 0.10% H_2O_2	3	Yes	16	21 ± 1	42.50
		0.500 M NH_4Cl + 0.005M $(NH_4)_2S_2O_8$	6	Yes	18	21 ± 1	21.0
		0.500 M NH_4Cl + 0.025M $(NH_4)_2S_2O_8$	1	No	17	21 ± 1	83.70
		0.500 M NH_4Cl + 0.05 M $(NH_4)_2S_2O_8$	1	No	17	21 ± 1	254.0
		0.500 M NH_4Cl + 0.20 M $(NH_4)_2S_2O_8$	1	No	18	21 ± 1	520.0

* Boiling in open beaker.

The attack of ammonium chloride on zinc itself is so slow that it can hardly be considered a stripping action. The time required to cause rusting of zinc plated iron samples intermittently immersed in ammonium chloride is sufficiently short that only a small fraction of the zinc would be removed if it were not for the oxidizing effect of the air. We have found that 120 hr. is as long a time as an intermittent immersion test using 2 per cent ammonium chloride generally requires to develop rust on flat plates carefully electroplated in the laboratory with a coating of 800 mg./sq. dm., which represents a thickness of about 0.0003 in. (0.0076 mm.) and is typical of thickness of zinc plated on iron for indoor service. This is a longer time than is generally required to develop rust on flat plates as they are commercially plated, and generally only a few hours are required for rusting irregularly shaped parts. Table I shows that an air-free, molar (5.3 per cent) ammonium chloride solution was found to attack zinc at the rate of 0.194 mg./sq. dm./hr., corresponding to 23 mg. in 120 hr., which represents only 3 per cent of the zinc coating on a sample having 800 mg./sq. dm. Even a 2 per cent solution of ammonium chloride, boiling in an open beaker, attacked zinc in a one hour test at the rate of 1.35 mg./sq. dm., and had the attack continued at the same rate for 120 hr., only about 20 per cent of a coating of 800 mg./sq. dm. would have been removed.

As a result of the foregoing observations ammonium chloride solutions were selected as a medium for use in the intermittent immersion test. After some experimentation we have found it convenient in our laboratory to use the particular apparatus described below. Thus far we have used this test only to evaluate zinc coatings electroplated on iron, but the relatively rapid rate of attack of zinc by ammonium chloride solutions containing small amounts of oxidizing agents (see Table I) suggests that the test may be useful in evaluating heavy zinc coatings such as are applied by a hot galvanizing process.

DESCRIPTION OF INTERMITTENT IMMERSION APPARATUS.

The samples ($S_1S_2S_3S_4$) are suspended from a movable rack (SR Fig. 1) which at regular intervals, as governed by a clock (CS), is lowered so that the samples are immersed in an ammonium chloride solution contained in 10-L. jars ($J_1J_2J_3J_4$), allowed

to remain there for 30 sec. and then raised and allowed to dry in the air for 15 min., when the cycle is repeated. The rack is raised and lowered by cables (C) attached to a drum (D) which is rotated first in one direction and then in the other by a motor-driven reversing gear (G_1). This reversing gear with its reducing gear (G_2) is of the type of assembly used in clothes washing machines, in which the drum rotates several times in one direction and then an equal number of times in the opposite direction.

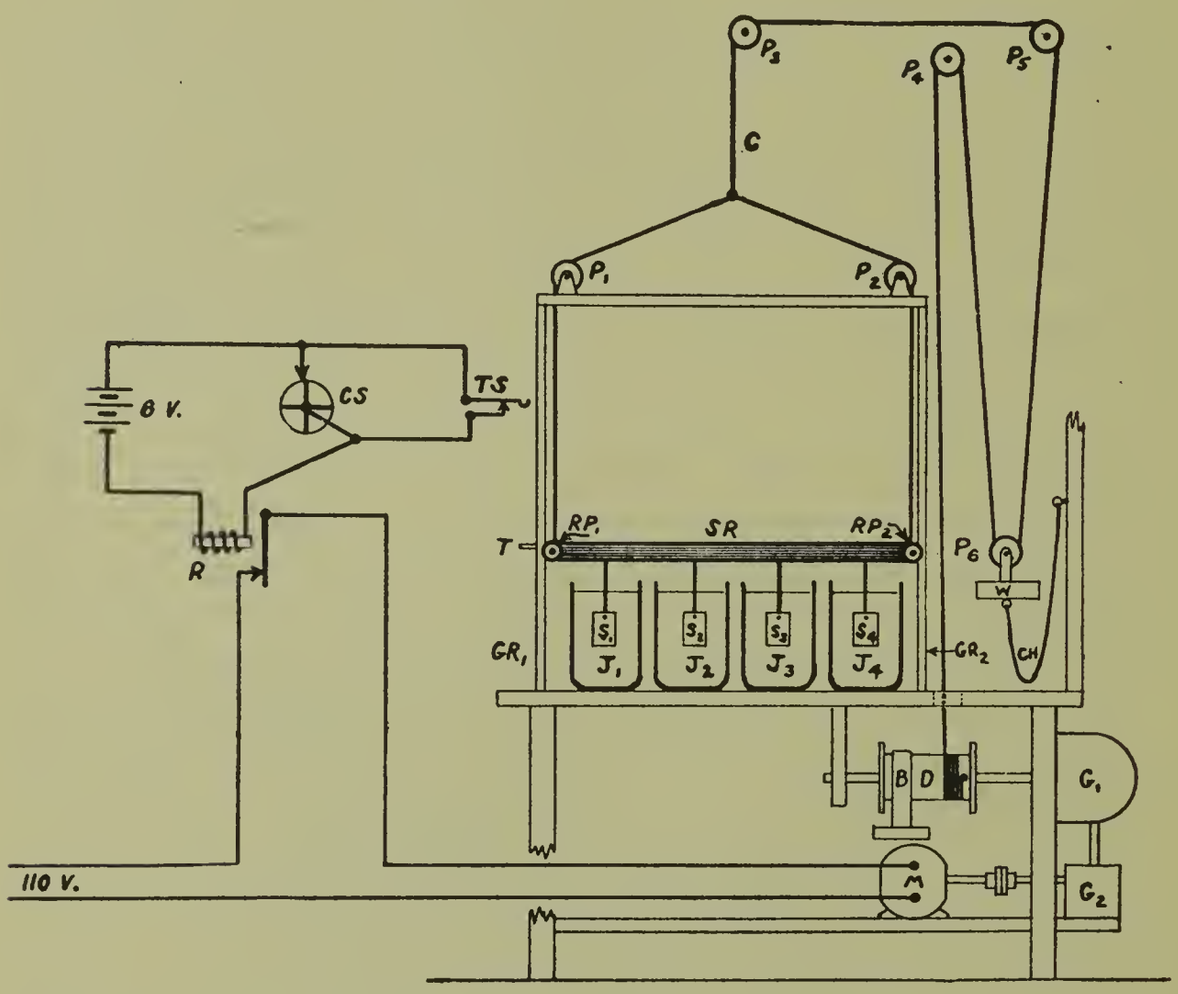

FIG. 1. Apparatus for Intermittent Immersion.

At each 15 min. interval the motor (M) is started by the clock, and the drum rotates six times in the direction of unwinding the cable. Since the testing rack is heavier than the movable weight (W) the rack lowers to a point where it is stopped by an adjustable stop on the guide rails (GR_1-GR_2), located so as to allow the samples to be completely immersed in the electrolyte.

As soon as the rack is stopped the movable weight lowers and takes up the slack as the cable continues to unwind. When the

reversing gear changes the direction of rotation of the drum, the weight carried on the movable pulley (P_6) rises to a point where the chain (CH) pulls taut and then the testing rack is raised to the point where the locking relay (TS) is opened by the trip (T) and the motor stopped. This completes a cycle of immersion and the samples dry in the air for 15 min. until the clock again starts the motor. The brake band (B) was found to be of value in maintaining a positive stopping of the cable drum at the time when the reversing gear changes its direction of rotation, and also to bring the testing rack quickly to rest when the motor current is broken at the completion of a cycle.

We have found it convenient to characterize the samples being tested by the number of cycles of immersion and drying before the appearance of visible rust. The number of cycles is recorded by a mechanical counting device. In carrying out our tests the samples are supported vertically from the lower edge by phenol-fiber clamps.

It has been our practice to use a 2 per cent ammonium chloride solution and change only when a test on a new lot of samples is started, unless it becomes badly discolored by rust. The range of time the solutions have been used has generally been three days to two weeks.

EVIDENCES OF THE VALUE OF THE INTERMITTENT IMMERSION TEST.

1. It provides a clearly observable indication (red rust) of pinholes that have been intentionally made in zinc coatings.

2. It will show thin spots in coatings at points where they are known to exist. This is illustrated by Fig. 2, which shows the type of corrosion produced on plates intentionally plated with thin spots at definite locations, and tested by intermittent immersion; (1) the two upper ones in ammonium chloride solution, and (2) the two lower ones in sodium chloride solution. The large circular spots on all four photographs are areas in which the plated coatings were intentionally made one-third as thick as obtained for the remainder of the plated surfaces. In the cases of the two plates tested in sodium chloride solution, the location of these thin spots has been artificially designated by marking concentric white and black rings on the negatives of the photographs; in the case of the plates tested in ammonium chloride, no

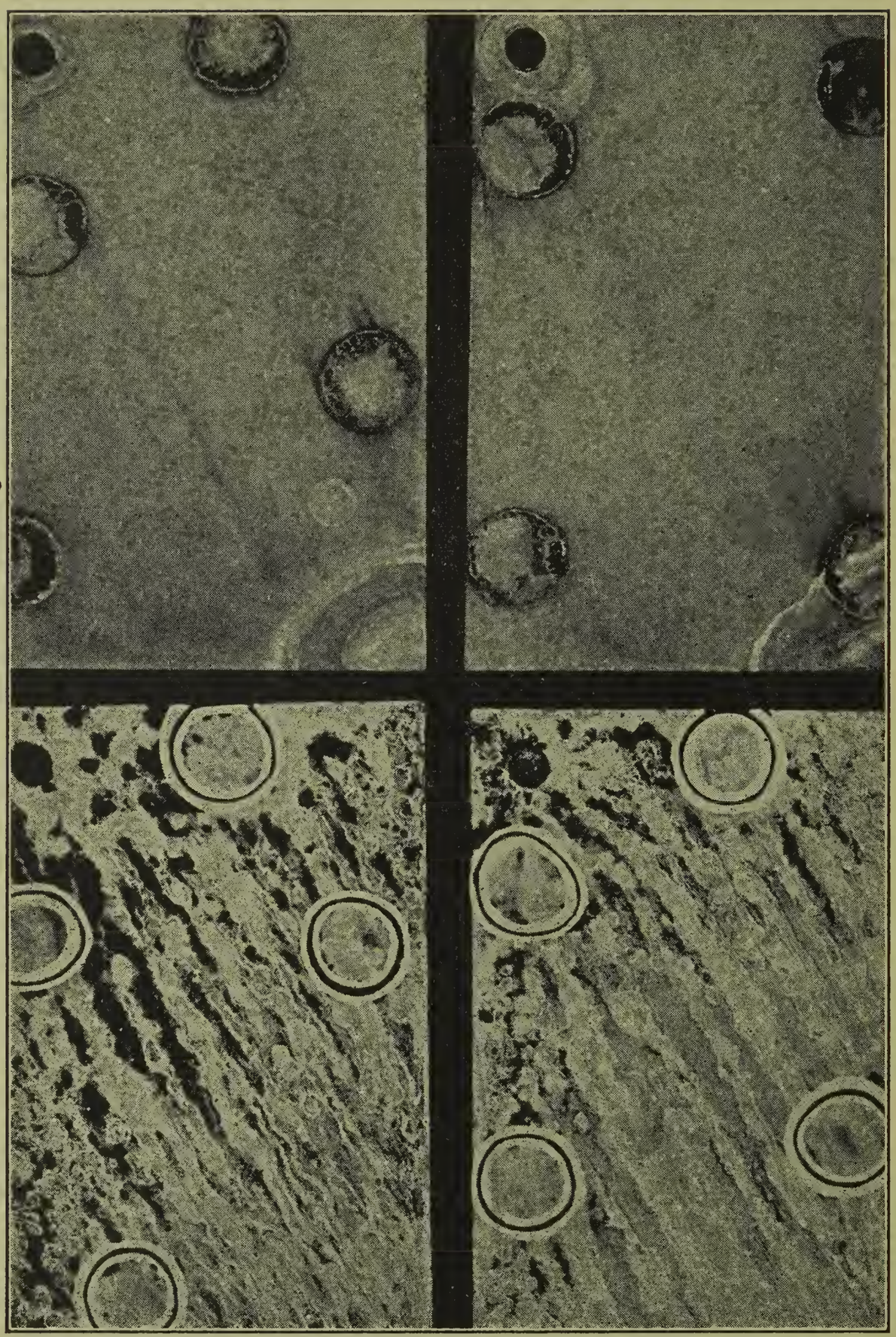

FIG. 2

artificial markings were used, since red rust appeared at the thin spots during the test to mark their location. In all four plates the dark spots in the upper left corners are holes in the plate from which they were suspended for plating and testing. Other than these holes and the black marking rings on the plates tested in sodium chloride, all black areas are actually rusted areas. The whitish incrustations occurring on the plates tested in sodium chloride are incrustations of salt and corrosion products.

As can be seen in the photograph, the surfaces of the plates tested in 2 per cent ammonium chloride remained free from corrosion products. Rust formed in the areas where the zinc coat was thinnest, but at no other point, not even in the area around the hole from which the plate was suspended in the plating solution.

The surfaces of the plates tested in 2 per cent sodium chloride were heavily incrusted with corrosion products, which streaked downward across the plates. Rust formed between the ridges of corrosion products, but curiously enough did not occur on any of the thin areas of the zinc plate.

These intermittent tests described above have been repeated with the same result. Likewise in our attempts to use the salt spray test to evaluate zinc plated coats on iron, we have not noticed any greater tendency for rust to appear first in the thinly plated areas (as recessed areas of irregularly shaped parts) than to appear on other areas which would be supposed to have received heavier plated coatings. These observations have led us to question the suitability of the salt spray test to pick weak spots in zinc plated coatings, particularly if the weaknesses are not marked.

The proposed test will cause the appearance of rust in recessed areas of plated parts, into which the deposited metal has not thrown well enough to produce coatings as thick as on areas located closer to the anodes in the plating bath. Table II illustrates this. The data given in this table are typical of tests repeatedly made, in which a large number of samples have been tested. In this table the last three columns give the number of cycles before the first appearance of rust. In the case of deep drawn parts this appearance of rust always occurs in the recessed area; in the case of angled parts, at the bottom of the angle, whereas on flat plates

the first appearance of rust is apt to be general over the entire surface.

3. The test shows the superiority of cyanide over sulfate zinc plating in a discriminating manner. Table II also illustrates this. The greatest disparity between these two types of plating is in the case of angled or recessed parts; but the test does show some superiority of the cyanide coat on flat surfaces as indicated.

4. The test can be used to discriminate between the effectiveness of different methods of precleaning parts to be plated. The condition of the surface produced by different methods of cleaning is reflected in the continuity of the plated coats. Any discontinuities that may exist in the coatings can best be detected by testing samples plated with comparatively thin coatings, as 150 mg./sq. dm. Table III illustrates this.

TABLE II.

Results of tests on parts of different types of surface plated from a sulfate or from a cyanide solution.

Type of Coating	Thickness of Coating mg./sq. dm.	Number of Samples	Average number of immersions before appearance of first rust		
			Deepdrawn Part	Angled Part	Flat Surface
Cyanide	155	5	21	97	195
Cyanide	620	5	168	345	632
Sulfate	775	5	10	27	559

In cleaning all of the samples listed in this table, the same method was used in removing grease and visible rust and scale, namely, alkaline electrocleaning to remove grease, followed by pickling in hot dilute sulfuric acid to remove visible rust and scale. After this treatment, so far as visual inspection was concerned, all samples looked uniformly clean. Before plating they were treated by the methods identified in the table as No. 1, 2, 3, and 4. Method No. 1 consisted of a bright acid dipping operation using a hot (90° C.) mixture of 50 per cent sulfuric acid, 25 per cent nitric acid, 25 per cent water. Methods No. 2, 3, and 4 were electrocleaning treatments differing from one another only in the concentration of

the cleaning agent, that used in No. 2 being the most concentrated. The data given in this table are typical of tests repeatedly made in which a large number of samples have been tested.

5. On parts of the same shape plated in the same manner, in the few observations we have made, rust was found to appear first in the same location, whether the parts were submitted to the accelerated test, to outdoor exposure or to conditions of warm humid atmospheres.

TABLE III.

Results of applying test to discriminate between methods of cleansing before plating

Cleaning Method	Thickness of coating mg./sq. dm.	Number of Samples	Average number of immersions before appearance of first rust		
			Deepdrawn Part	Angled Part	Flat Surface
No. 1	155	5	32	54	224
No. 2	155	5	24	83	223
No. 3	155	5	21	51	209
No. 4	155	5	12	41	194

We do not feel that we can claim, on the basis of the present limited experience, that the proposed intermittent immersion test enables one accurately to predict the useful life of zinc plated iron under any particular condition of service; but we do feel that it is of considerable value in judging whether or not a satisfactory plate has been applied to any part inspected, and probably of some value in judging the serviceability of zinc plated iron or steel.

In this paper the authors have confined themselves to a discussion of a method for the rapid evaluation of zinc coatings, and have not discussed the theoretical aspects of the corrosion of zinc, nor included a survey of the numerous corrosion data to be found in the literature.

The authors wish to express their thanks to Dr. R. M. Burns of this Laboratory, for obtaining the data shown in Table I, and to Mr. A. H. Kopp for aid in designing and building the apparatus herein described.

DISCUSSION.

C. J. WERNLUND[5]: Through the courtesy of Mr. Farnsworth and Dr. Hocker, we have had this intermittent immersion test in operation for the past five months, and have found it very useful in evaluating the relative life of various types of zinc and zinc mercury alloy deposits upon steel. Our results with sulfate and cyanide deposits check those reported in this paper.

Since the immersing apparatus used by us differs radically from that described in the above paper, it may be of interest to describe it briefly.

The immersing member consists essentially of a bicycle chain about 15 ft. (4.6 m.) long, supported on three 10-tooth sprockets set in a vertical plane so as to form a right-angled triangle with one of the acute angles coming just above the surface of the ammonium chloride solution. Twenty hard rubber immersing rods, 4 x 5/8 x 5/8 in. (10.2 x 1.6 x 1.6 cm.), are bolted to the chain so as to form right angles with it, and protruding 3.5 in. (8.9 cm.). The test samples are attached to the free ends of the hard rubber rods by zinc-plated screws. A 20 L. enamelware tank containing the 2 per cent ammonium chloride solution is set directly below the lowest sprocket. The height of the ammonium chloride solution and the speed and length of the chain are so adjusted that the samples are immersed in the ammonium chloride solution for 20 sec. and then exposed to the air for 15 min. This chain with its test samples is chain-driven by a 1/30 horse power motor geared down 900 times by means of two small worm gears.

COLIN G. FINK[6]: One of the most important points brought out in the paper is the value of the intermittent test. It is a curious thing that some coatings when exposed to the salt spray test, for example, a thin coating of silver will form a coating of silver chloride, which protects the rest of the silver pretty well. However, if you take that sample and allow the silver chloride to decompose in the air and then expose it again to the salt spray, you have an intermittent test and will get an entirely different result. It is important to imitate actual service of a plated sample,

[5] The Roessler and Hasslacher Co., New York.

[6] Head, Division of Electrochemistry, Columbia Univ., New York City.

and that makes this new test particularly valuable. I think it would be well worth while for others who are strong believers in the salt spray test, and who consider anything that does not stand up by the salt spray test as being unfit for service, to take account of this new test.

W. Blum[7]: It would be of interest to know how much of the difference in the two tests was dependent upon the use of ammonium chloride, and how much upon the intermittent immersion. Do the authors know whether ammonium chloride has ever been used in the spray test, and whether it has any advantages over sodium chloride?

C. D. Hocker: No, we have made no tests along those lines. It is, however, my judgment that one is more often able to rig up a simple apparatus for moving parts in and out of solution than he may be to supply himself with compressed air. Also, I think this kind of a test is, perhaps, more fool-proof in its operation, because the only requirement is dipping parts in and out of a solution, and there is no problem of adjusting a spray so that it is directed in the proper way toward the samples. As regards the particular apparatus described in our paper, we do not feel that it may be any better than similar kinds of apparatus that might be devised for convenient use. Our company sells washing machines, and we had a washing machine gear assembly available.

M. R. Thompson[8]: Mr. Wernlund has given us a parallel connection between his own salt spray and atmospheric corrosion tests, and has mentioned, if I understand him correctly, that there was also a good parallelism between the Farnsworth and Hocker test conducted at New York and the one at Perth Amboy. Can he give us a further connection between his experience with the salt spray and the Farnsworth and Hocker tests? Did they give the same results or not? That seems to be the point at issue.

C. J. Wernlund: Yes, they agree quite closely.

M. R. Thompson: Exactly how closely do they parallel the Farnsworth and Hocker test?

C. J. Wernlund: We only tried the Farnsworth and Hocker test in the case of flat steel sheets, and we found that while the number of hours was shortened somewhat in the new test for a

[7] Chemist, Bureau of Standards, Washington, D. C.
[8] Bureau of Standards, Washington, D. C.

given weight of coating, if we figure comparative resistances on a percentage basis, the results varied less than 10 per cent.

M. R. THOMPSON: There seems to be pretty good concordance between the salt spray test and the Farnsworth and Hocker test.

C. J. WERNLUND: Yes. The superiority of the new test lies in the fact that it is more discriminating. For example, electrolytic "zinc anode-cyanide" deposits and the "prime Western zinc anode-cyanide" deposits in a salt spray test give us very closely the same results. We are able to distinguish a 5 to 10 per cent superiority for the electrolytic anode deposits by this test, which we are not able to do in the salt spray test.

R. J. MCKAY[9]: Is this last result also checked by the results of atmospheric corrosion?

C. J. WERNLUND: Yes. The Farnsworth and Hocker method checks the atmospheric corrosion somewhat closer, as far as we were able to find out, than the salt spray test.

COLIN G. FINK: The parallelism that Mr. Wernlund found in the case of the salt spray test and in the Farnsworth and Hocker test applies in the case of zinc, but it does not necessarily apply to other metals, and my statement still holds good that personally I consider this intermittent test much more reliable as a general test than I do the salt spray test.

E. M. BAKER[10]: In studying the salt spray resistance of nickel-plated steel,[11] we found that the way in which the piece approached a noticeably rusty stage might not correspond to the time of the first appearance of rust. That is, of a number of specimens tested simultaneously, the specimen on which rust may first be detected is not necessarily the specimen which will first become noticeably rusted. Because of this, we found it necessary to work out an arbitrary method of rating, to take into account both the way in which the specimens progressed to a noticeably rusted stage, and the number of hours required to reach that stage. It is not at all improbable that the Farnsworth and Hocker immersion test would be free from this discrepancy. I had the privilege of seeing some samples at Dr. Hocker's laboratory, and these are quite convincing as to the superiority of the immersion test, at least for zinc coatings.

[9] International Nickel Co., New York City.
[10] Dept. of Chem. Eng., Univ. of Michigan, Ann Arbor, Mich.
[11] Rust Resistance of Nickel-plated Steel, J. of the Soc. of Automotive Engrs., 14, 127.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

A FURTHER STUDY OF THE DEZINCIFICATION OF BRASS.[1]

By Cleveland F. Nixon[2]

Abstract.

The presence of oxygen or of comparatively highly ionized copper in solution is necessary to initiate selective corrosion. The acetate, lactate, bromate, and perchlorate of copper do not promote dezincification. Brass is not the only alloy susceptible to "dezincification"; copper-aluminum (70-30), manganese-copper (25-75), and cadmium-magnesium (85.7-14.3) were found subject to selective corrosion. From experimental evidence it is concluded that, with the exception of 90 per cent, or more, copper alloys, the commercial brasses are subject to dezincification. Of the special alloy brasses tested arsenic brass and nickel brass are recommended for further study.

In a recent paper[3] Ralph B. Abrams explained the mechanism by which the dezincification of brass is accomplished. He came to the conclusion that the phenomenon of dezincification is not caused by the leaching out of the zinc, nor is it primarily the result of couples set up between the copper and zinc particles. Instead he found dezincification to be the result of the dissolving of the brass as a whole with the subsequent redeposition of the copper. Furthermore, he found that there is no dezincification whatsoever unless a membrane, either natural or artificial, is present to hold the copper-rich solution in contact with the brass.

It is the purpose of the present paper to build on the foundation Mr. Abrams has laid. Corrosion tests have been made upon the whole gamut of commercial brasses and bronzes, in an effort to discover a brass that is not susceptible to dezincification by sea

[1] Manuscript received July 5, 1923.

[2] Dept. of Chemical Engineering, University of Wisconsin, Madison, Wis.

[3] Trans. Am. Electrochem. Soc., 42, 39 (1922).

water. Before taking up this phase of the investigation, however, it will be well to review some of the work done on 70-30 sheet brass from the same piece from which Mr. Abrams secured his specimens, and also on some specially made alloys, in order to bring out limitations of the rapid corrosion method, and to bring out more evidence in regard to the problem of selective corrosion.

ROLE OF OXYGEN IN DEZINCIFICATION.

The solutions used during the investigation, usually 150 to 250 cc. in volume, were contained in ordinary glass tumblers covered with watch glasses to minimize evaporation and to keep out dust. Since the type of corrosion which is particularly troublesome to users of brass is dezincification rather than corrosion as a whole, no attempt has been made to conduct quantitative tests.

The solutions given in Table I were boiled and sealed with oil to exclude oxygen.

TABLE I.

Action When Oxygen is Excluded.

Expt. No.	Time in days	Solution	Result
1	17	H_2SO_4—0.5*N* $CuSO_4$—0.5*N*	The dezincified specimen was covered with bright copper crystals and occasional areas of smooth brass skin. The dezincification was more extensive at the strained portion of the bent brass strip than at the unstrained portion.
2	17	HCl—0.5*N* $CuCl_2$—0.5*N*	Same as Exp. 1.
3	85	HCl—0.5*N* NaCl—0.5*N*	No dezincification whatsoever.

In experiment No. 3, at the end of 85 days, 5 cc. of hydrogen peroxide was introduced below the surface of the oil. Under this new condition appreciable dezincification occurred within 38 days. In other tumblers, using solution No. 3, it was found that the addition of only 1 g. cupric chloride or the bubbling of air through the solution produced a similar result.

Thus it is apparent that oxygen plays no part in the dezincifica-

tion of brass in copper solutions, which is as would be expected. Copper is slowly deposited and brass, as such, goes into solution. In this respect the action resembles immersion plating.

However, in solutions which contain no copper, the action is different. The copper which is necessary to start dezincification is dissolved with an evolution of hydrogen. Since the discharge potential of hydrogen on brass is higher than the potential of brass itself, oxygen is needed as a depolarizer. Once started, however, the process of dezincification is capable of continuing without access of oxygen.

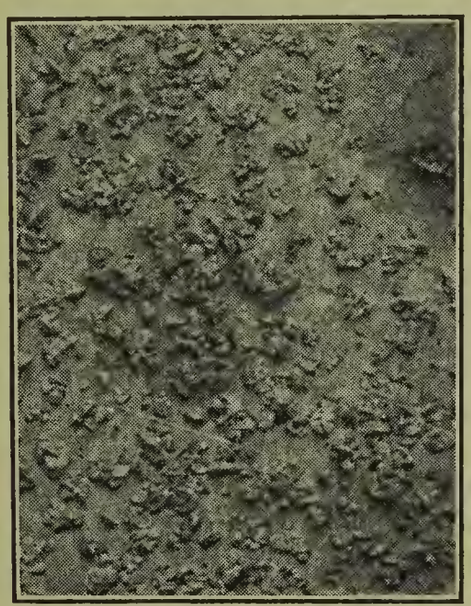

FIG. 1.

FIG. 2.

Figures 1 and 2 show crystals of copper which form on the surface of brass during dezincification. These photographs are of samples of hard 70: 30 brass, subjected to chemical corrosion in cupric chloride solution acidified by hydrochloric acid. The crystals consist of solid copper with a brilliant, metallic luster. Such crystals occur in both chemical and electrolytic dezincification of brass, in copper solution.

THE EFFECT OF VARIOUS COPPER SOLUTIONS.

Up to this time the only salts that had been used were the sulfate and the chloride. It was assumed that any soluble copper salt, since it is at least slightly ionized, would furnish copper to be deposited, and would therefore initiate dezincification.

To verify this assumption 70-30 sheet brass was subjected to the action of all the copper solutions available. Of these it was found, in addition to the sulfate and chloride, that the nitrate and the fluosilicate produce dezincification. But the acetate, cold or heated to 80° or 90°, the lactate, the acetate plus potassium bro-

mate, and the perchlorate, all acidified with the corresponding acid, after 80 days, produced not the slightest trace of dezincification.

It was at first thought that this most unexpected difference in the effect of various copper solutions was due to a change of potential of copper with respect to brass, in the different solutions. Experiment showed that this was not the case; indeed the difference in potential between copper and brass is greater in acetate solution than in sulfate. It is noticeable that those salts which foster dezincification are, relatively speaking, excellent conductors, while those which do not dezincify brass are poor conductors. It appears, furthermore, that the degree of ionization influences selective corrosion of brass. Since copper may be plated electrolytically from any of these solutions, it is difficult to see why plating by immersion will not also take place when the opportunity to do so is offered.

THE SKIN OF BRASS.

Perhaps the most puzzling phenomenon encountered during this investigation was a thin skin of brass which appeared, with few exceptions, upon every specimen studied. As far as this skin is concerned, it is immaterial whether or not the solution used is chloride, sulfate, nitrate, or fluosilicate, whether copper is present in the solution or absent. To the above generalization two exceptions are to be noted—brass in cupric chloride plus potassium dichromate, and brass in cuprous chloride dissolved in a solution of magnesium chloride and hydrochloric acid. In these cases, corrosion as a whole as well as selective corrosion takes place. Where dezincification alone has occurred, and where the skin of brass is present, the original size and shape of the specimens are retained.

The skin itself is composed of shiny brass, sometimes easily peeled off and sometimes tightly adherent. It is very thin (estimated 0.0078 in. (0.02 mm.) or thinner) and is continuous except for places where crystals of copper occur. On some specimens crystals covered the entire surface exposed. These copper crystals grow up through small openings in the brass film and gradually spread over the surface; where the film has been thus covered it is usually eliminated by dezincification.

It has been suggested that this skin acts as a membrane which holds the copper solution in contact with the brass beneath, and so makes dezincification possible. But if this were true, the skin also should be destroyed, for such a corrosive solution may be expected to bore outward as well as in. The skin, it must be concluded, is, in electrical potential, or in some other unknown way, different from the rest of the brass.

SELECTIVE CORROSION OF ALLOYS OTHER THAN BRASS.

Monel Metal

Monel metal was subjected to the tests used in studying brass, namely chemical and electrolytic corrosion in acidified copper sulfate, acidified sea water, and acidified cupric chloride. In no case did selective corrosion take place, although the loss by ordinary corrosion was, in 224 days, 0.065 g. per sq. cm. in acidified sea water and 0.04 g. in copper sulfate. Monel metal undergoes no action comparable to the dezincification of brass, nor, it may be added, does German silver. These facts are easily explained by the fact that both Monel metal and German silver are lower in the scale of potentials than copper.

Special Alloys.

Several special alloys were made to determine whether or not the phenomenon of selective corrosion could be obtained with alloys other than brass. Theoretically, any solid solution made up of metals widely different in potential should, when placed in an appropriate solution, show "dezincification." As far as this conclusion was tested it proved to be true.

A copper-aluminum alloy containing 70 per cent copper and 30 per cent aluminum, though very brittle and highly crystalline, was found to be even more susceptible to selective corrosion than is brass. "De-aluminification" was induced by a solution of copper acetate and acetic acid. A manganese-copper alloy (25 per cent manganese and 75 per cent copper) was found to undergo selective corrosion in the same manner as does brass and aluminum-copper.

As a copper-free alloy which should undergo selective corrosion, an alloy of 85.7 per cent cadmium and 14.3 per cent magnesium was made. Two samples of this alloy, one unwrapped, the

other swathed in several layers of filter paper were placed in an acidified solution of cadmium chloride and allowed to stand for 48 days, with the following result:

(a) The unwrapped specimen was found to be swelled completely out of shape. Originally, it was an inch (25 mm.) section of a half-inch (12.5 mm.) circular bar, but at the end of the experiment, it was almost spherical. Except for a small core of the original metal at the center, the entire mass was spongy, crumbly, black cadmium.

TABLE II.

High Copper Brasses and Bronzes.

Exp. No.	Time in Days	Composition Per cent	Dezincification	Remarks
1	17	Cu 90 Zn 10	None	Temper, soft; corrosion as a whole, considerable.
2	26	Cu 94.88 Zn 5.08 Pb trace Fe 0.04	None	Some corrosion.
3	33	Cu 92 Pb 8 Fe 0.25	None	Temper, soft (sheet). Specimen covered with layer of tightly adherent black copper oxide. Some corrosion.
4	33	Cu 92 Pb 8 Fe 0.25	None	Temper No. 6, hard (sheet). Specimen covered with layer of tightly adherent black copper oxide. Some corrosion.
5	48	Cu 88 Sn 10 Zn 2	None	Gun metal; this specimen was also run in acidified $CuSO_4$, and electrolytically in sea water, with the same effect. Slight corrosion.
6	46	Cu 90 Fe 2 Al 8	None	Ampco bronze (sheet). Much corrosion. Also run electrolytically with similar results.

(b) The original shape of the wrapped sample was preserved. On unwrapping, it was found that a few gray crystals had grown up through a small break in the paper, just as copper crystals grow up through the brass skin. The specimen itself was covered

TABLE III.

Copper-Zinc Brasses.

Exp. No.	Time in days	Composition Per cent	Temper and Form	Dezincification	Remarks
7	28	Cu 80 Zn 19.84 Fe 0.04 Pb 0.1	Hard sheet	None.	A black powder on the specimen, probably copper oxide. Some corrosion.
8	26	Cu 79.55 Zn 20.40	Soft rod	In sections.	Black powder on specimen.
9	26	Cu 79.00 Zn 20.95	Hard sheet	Thin, tightly adherent copper film.	No oxide or brass film on surface of specimen.
10	33	Cu 60.00 Zn 39.19 Fe 0.09	Soft sheet	Copper crystals and a loose, continuous jacket of copper.	The copper deposit readily peeled off, showing pitted yellow brass beneath.
11	33	Cu 61.00 Zn 38.88 Pb 0.07 Fe 0.05	Hard rod	Some.	The original surface of the brass is very resistant to corrosion. All the dezincification took place at the sawed ends.
12	33	Cu 61.50 Zn 38.24 Pb 0.21 Fe 0.09	Hard rod	Some at ends as before.	The specimen was also run in acidified $CuSO_4$. At the end of 63 days the piece was covered with dense copper crystals and brass skin, under which was considerable redeposited copper.
13	30	Cu 63.00 Zn 36.88 Pb 0.07 Fe 0.05	Hard tube	Unaffected save on outside edges.	Was also tested in acidified $CuSO_4$ solution with a result similar to that obtained in the case of Exp. 12. The copper solution was much paler blue at the end of the test than at the beginning.
14	30	Cu 65.50 Zn 34.23 Pb 0.21 Fe 0.06	Hard sheet	Copper crystals.	The brass skin was over about 0.02 mm. of re-deposited copper.
15	30	Cu 69.96 Zn 29.99	Hard rod	Fine crystals; very little dezincification.	
16	33	Cu 61.74 Zn 38.16 Pb 0.10 Fe 0.04	Soft rod	Faint trace on ends.	The protective action of the tough outer layer was particularly noticeable in this specimen.

with gray metallic crystals, and partially, by the original shiny surface. This shiny surface was only a film easily removed, showing a black amorphous material below.

Three things are noteworthy here. First, there is a skin effect, such as is observed in the dezincification of brass; second, the action is much more rapid than in the case of brass; and third, the effect of the membrane is to retard the action, rather than to

TABLE IV.

Leaded Brasses.

Exp. No.	Time in days	Composition Per cent.	Temper and form	Dezincification	Remarks
17	12	Cu 60.00 Zn 37.50 Pb 2.50		Dense continuous copper envelope.	Electrolytically as anode in sea water. Current density 0.3 amp./sq. ft. (0.03 amp./sq.dm.) No brass skin.
18	30	Cu 65.50 Zn 33.32 Pb 1.12	Hard sheet	Along edges, but only a few crystals on surface.	The tough outer layer of brass affords protection against corrosion.
19	30	Cu 67.75 Zn 31.06 Pb 1.13	Soft sheet	Along edges, but only a few crystals on surface.	Evidently the effect of heat treatment is here very slight.
20	32	Cu 63.75 Zn 34.19 Pb 2.00	Soft rod	Along edges, but only a few crystals on surface.	
21	32	Cu 63.75 Zn 34.19 Pb 2.00	Hard rod	No dezincification appreciable.	Here temper seems to have some influence.

speed it up as is the case with brass. This last may be explained only by assuming that the close packing of the redeposited metal enforced by the artificial membrane retarded the passage of solution into the metal. This reasoning, carried further, will explain why brass corrodes so much more slowly than the magnesium-cadmium alloy. Re-deposits of copper are, as a rule, quite dense and continuous; seepage through this material is necessarily, therefore, a slower process.

Thus it may be seen that brass is by no means the only alloy which undergoes selective corrosion. However, all alloys which are subject to "dezincification" have one property in common. They may be said to contain within themselves the seeds of their own destruction. That is, one of the salts formed by corrosion turns about and attacks the original alloy.

TABLE V.

Commercial Tin-Brass.

Exp. No.	Time in days	Composition Per cent	Temper and Form	Dezincification	Remarks
22	83	Cu 60 Zn 39 Sn 1		Slight but uniform coat of copper over entire specimen.	Naval brass. Result verified by using as anode in sea water.
23	123	Cu 70 Zn 29 Sn 1	Light annealed	The merest trace of dezincification.	Admiralty brass. Result also checked by using as anode in sea water.
24	33	Cu 62 Zn 37 Sn 0.75 Fe 0.08	Hard tube	A few copper crystals on the surface of the metal, but that is all.	
25	30	Cu 62 Zn 37 Sn 0.75 Fe 0.08	Soft tube	Much of the specimen has completely corroded away, but especially toward the bottom of the piece there is considerable dezincification.	This specimen and specimen 24 are identical in composition. Annealing in this case effects an increase in dezincification.

COMMERCIAL BRASSES AND BRONZES.

All of the experiments recorded in Tables II, III, IV and V are chemical corrosion tests in a solution half normal to both hydrochloric acid and sodium chloride, unless otherwise stated.

It is seen from Table III that ordinary brasses succumb uniformly to dezincification.

It is evident from Table IV that, as far as dezincification is concerned, the presence of one or two per cent of lead is immaterial. The results recorded in Table IV, and for straight brasses, in Table III, are almost identical.

The tin brass stands up better, perhaps, than any of the other brasses, but still leaves much to be desired. There is no commercial brass that, from our tests, could be expected to stand up indefinitely without dezincification. The next step, therefore, was to attempt to secure an alloy that would resist dezincification. The first of these to be considered is nickel brass.

TABLE VI.

Nickel Brass.

Exp. No.	Time in days	Solution	Per cent Nickel	Dezincification
26	27	0.5*N*HCl; 0.5*N*NaCl	4	None
27	27	Acidified $CuSO_4$	4	None
28	12	Electrolytically, as anode, in sea water	4	None
29	27	0.5*N*HCl; 0.5*N*NaCl	8	None
30	27	Acidified $CuSO_4$	8	None
31	12	As anode in sea water	8	None

NICKEL BRASS.

Attention was drawn to nickel brass by the fact that German silver, (Ni 18 per cent, Cu 64 per cent, and Zn 18 per cent) resisted all efforts to bring about dezincification. Two alloys were therefore made with copper and zinc in the ratio of 60-40, one containing 6 per cent nickel, and the other 4 per cent nickel. These were subjected to chemical corrosion in the hydrochloric acid and salt solutions, with the results shown in Table VI.

These results are promising. Since there was not the slightest indication of dezincification in any case, it is probable that the percentage of nickel can be further cut down without altering the resistance of the alloy to dezincification. This will be an interesting alloy to study further.

SILICON BRASS.

It was thought that silicon might prevent the dezincification of brass. So two alloys, one containing 1 per cent and the other 2.5

per cent, of silicon were made from 70: 30 brass and the element silicon. These alloys were tried out in all the standard solutions, both chemically and electrolytically, and appear to be on a par with tin-brass in regard to dezincification, except for this curious fact: for silicon brass, acid chloride solution is without effect while copper sulfate is very corrosive. In the case of the tin-brass this is reversed. The tin alloy is more susceptible to the action of the hydrochloric acid-salt solution, but withstands the action of sulfate solutions for days without visible change. Silicon brass should prove useful in sea water if its physical properties are acceptable.

ANTIMONY BRASS.

A brass containing less than 0.5 per cent of antimony was tested, but found to be of no value. Antimony in this quantity has practically no influence upon dezincification. The attempt to utilize antimony was inspired by the fact that arsenic brass proved to be so remarkably resistant.

TABLE VII.

Arsenic Brass.

Solution	Time in Days	Dezincification
0.5*N* NaCl ..... 0.5*N* HCl	85	None
0.5*N* $CuSO_4$ ..... 0.5*N* H_2SO_4	29	None
Acidified $CuSO_4$	32	None
Sea water, as anode	12	None

ARSENIC BRASS.

Following the suggestion of G. D. Bengaugh and R. May in a communicated discussion of Abrams' paper on the dezincification of brass, an alloy containing less than 0.3 per cent of arsenic was made up; the results, recorded in Table VII, were remarkable.

It is evident that arsenic plays a remarkable part here, as it does in many other cases. A slight addition of arsenic to a dilute solution of sulfuric acid will nearly stop the corrosion of iron in

this solution. By dipping iron or steel into a solution of arsenic in dilute hydrochloric acid, deposition by immersion of copper from a solution of copper sulfate will be stopped.

From the above experiments it is apparent that a small fraction of one per cent of arsenic in brass will greatly retard, if not completely prevent, dezincification. While this beneficial effect is explainable where hydrogen is evolved in corrosion, in the case of brass the mechanism is not apparent.

In the preparation of this paper, indebtedness is acknowledged to E. D. Coleman, who started this investigation, to William Price, chief chemist of the Scovill Co., Waterbury, Conn., for his co-operation in furnishing samples of some thirty commercial brasses; and especially to Professor O. P. Watts, without whose suggestions and guidance this paper would never have been written.

CONCLUSION.

1. Oxygen or an appropriate copper salt in solution is essential to start the dezincification of brass.

2. Solutions of copper acetate and other slightly ionized salts do not incite the dezincification of brass.

3. Monel metal and German silver proved entirely resistant to selective corrosion. This finding is corroborated by experience. Monel has been used extensively and successfully for marine fittings.

4. The condition of the surface is an important factor in dezincification. Whether or not the surface offered to corrosion is the original cast or rolled surface, or has been recently fractured, filed or cold-worked, sometimes determines whether or not dezincification will occur.

5. Brass, though the only commercial alloy subject to dezincification, is by no means the only alloy susceptible to this type of corrosion.

6. The rate of dezincification is dependent to a considerable extent upon the porosity of the redeposited metal.

7. All alloys tested containing above 90 per cent of copper were not subject to dezincification, no matter what constituents made up the other 10 per cent.

8. In general, commercial brasses are all subject to dezincification; heat treatment and the presence or absence of the beta constituent are only minor details. Tin, however, slows down the action to a considerable extent.

9. Antimony brass is of little use in resisting dezincification; silicon is beneficial in slowing down selective corrosion in sea water; while nickel and arsenic brasses appear promising, and are worthy of special study.

DISCUSSION.

C. H. ELDRIDGE[4]: In the past year we made some observations that check Mr. Nixon's statement that other alloys besides brass are susceptible to this selective corrosion or dezincification. While working with specimens of ancient bronze and silver, for the Metropolitan Museum in New York, we studied two ancient bracelets covered with a hard, green, oxy-chloride crust and classified as bronze. On removing the crust we brought to light a smooth, white metallic core, which proved to be silver.

It seems that the copper, alloyed with the silver as a hardener, had migrated outward under the corrosive influences of the moist soil, and the final product was a spongy silver core covered with a high copper crust. One bracelet, when finished, was about the size of a lead pencil and was hard and strong. The other bracelet was completely decuperized, leaving a soft, spongy core of silver with no ductility or mechanical strength. I remember to my disappointment that I tried to bend it a little, but it snapped like a pipe stem. Thus we have two cases where sterling silver or copper-silver alloys will undergo selective corrosion.

COLIN G. FINK[5]: It is only by the removal of the green copper crust, by a new process which we devised, that we find the silver and observe that the copper in the alloy has moved outwards, leaving the silver behind. Whether or not the separation of the copper from the silver takes place in two stages, whether

[4] Research Metallurgist, Metropolitan Museum of Art, New York City.
[5] Head, Division of Electrochemistry, Columbia Univ., New York City.

or not both the copper and the silver go into solution first and the silver is then precipitated out again, or whether it is merely the copper going into solution and forming the crust, we really do not know. Personally, I am inclined to believe that both metals go into solution and that metallic silver is precipitated out as a secondary reaction. At all events, as Mr. Eldridge said, the decuperization of our copper-silver alloy fits in nicely with Mr. Nixon's study of the dezincification of brass.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

THE MEASUREMENT OF DECOMPOSITION POTENTIALS.[1]

By Alfred L. Ferguson[2] and Gerrit Van Zyl.[2]

Abstract.

In this investigation an apparatus is developed, by which a direct comparison is made between all the values obtained by the commutator and direct methods for measuring decomposition potential and overvoltages. Evidence is given which should help materially to settle the controversy, which has so long existed concerning the relative merits of these two methods. All measurements made by the commutator method are averages, and depend to a large extent upon the operation and mechanical construction of the commutator.

Two methods have been employed extensively for the determination of decomposition potentials and overvoltages. The first, called the direct method, was suggested by Fuchs[3] in 1875, and was later used by Caspari,[4] Coehn and Dannenberg,[5] Möller,[6] and many other investigators. The second, or commutator method, in which a rotating commutator is used, was suggested by LeBlanc[7] and later used by Pring[8] and others, but especially by Newbery.[9]

Opinions differ as to which of the two methods of measurement gives true overvoltage values. J. M. Pring states that the

[1] Manuscript received February 15, 1924. The work herein reported is a portion of the thesis presented by Gerrit Van Zyl to the faculty of the graduate school of the University of Michigan in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Chemical Laboratory, Univ. of Michigan, Ann Arbor, Mich.

[3] Pogg. Ann., 156, 158 (1875).

[4] Z. phys. Chem., **30**, 89 (1899).

[5] Z. phys. Chem., **38**, 609 (1901).

[6] Z. phys. Chem., **65**, 226 (1909).

[7] Z. phys. Chem., **5**, 469 (1890).

[8] Pring and Tainton, J. Chem. Soc., **105**, 712 (1914); Pring, Z. Elektrochemie, **19**, 255 (1913).

[9] J. Chem. Soc., **105**, 2419 (1914); Man. Men. Lit. and Philo. Soc., **60**, No. 11 (1916), also **61**, No. 9 (1917).

disadvantage of the direct method is that the values contain not only the polarization potential, but also the additional potential which is due to the "transfer resistance" between the electrode and electrolyte during the passage of the current. He favors the commutator method, since in his opinion it gives the true value for polarization potential or "back e. m. f."

Newbery maintains that the direct method gives true overvoltage values only at extremely low current densities, while at high current densities the values obtained are erroneous, because the potential necessary to overcome the resistance of a film of gas around the electrode is included in the measurements. The work of MacInnes and Adler,[10] and MacInnes and Contieri[11] on hydrogen overvoltage, in which they use the direct method with slight modification, is severely criticised by Newbery[12]. W. R. Mott[13] states that the use of a rotating commutator often introduces errors due to capacity effects. Bennett and Thompson,[14] in their discussion of overvoltage, consider only values obtained by means of the commutator method. Chaney[15] criticises Bennett because he calls overvoltage, as he defines it, "true overvoltage," and overvoltage phenomena which arise from resistance and capacity effect, "false overvoltage."

A point which deserves special mention is that the discharge potential has usually been measured too soon (in some cases only half a minute) after the charging potential was applied or increased. Another question is the proper rate of rotation of the commutator. LeBlanc[16] used a commutator rotating at the rate of 1200 to 1500 r. p. m. Newbery states that when the rate of rotation is 1000 r. p. m., or more, there is no change in the overvoltage, and that the fall of discharge potential in 1/2000 of a minute is negligibly small.

From an analysis of the existing literature on decomposition potentials the authors felt convinced that both methods contained so many elements of uncertainty, and that the subject of overvoltage measurement is so indefinite that an intensive study of

[10] J. Am. Chem. Soc., 41, 194 (1919).
[11] J. Am. Chem. Soc., 41, 2013 (1919).
[12] J. Am. Chem. Soc., 42, 2007 (1920).
[13] Trans. Am. Electrochem. Soc., 29, 181 (1916).
[14] Trans. Am. Electrochem. Soc., 29, 269 (1916).
[15] Trans. Am. Electrochem. Soc., 29, 181 (1916).
[16] Z. phys. Chem., 5, 469 (1890).

the whole question was essential before it could be considered a reliable method of electrochemical investigation. They were inclined to ask the same question which MacInnes did in his article, why should there be any difference between the values obtained by the two methods? An answer to this question should settle the controversy concerning the use of these methods.

The first task was to develop a set-up which would permit measurements whereby all of the various questionable features in connection with decomposition potential measurements could be accurately studied. Such a set-up must permit measurements to be made by both methods at the same time and under identically the same conditions.

APPARATUS AND METHOD.

The apparatus as finally arranged is shown in Fig. 1. The charging circuit consists of a storage battery BA′, line switch IV, and a variable resistance R + R′. Any desired potential can be tapped off by changing the relative resistances in R and R′, and can be applied to the electrolytic cell. A milliammeter, A, is connected in series with the cell to determine the current. In the later work this is replaced by a standard resistance. The potential measurements are made by means of a Leeds and Northrup student type potentiometer. The leads from the potentiometer set-up are connected through the galvanometer, Ga, and key, K, to the middle of the reversing switch, I. The Weston standard cell, V, is the standard for comparison of all measurements. A standard normal calomel electrode, a and b, is placed directly behind each of the two platinum electrodes, +Pt and —Pt.

For the benefit of the reader who may wish to trace the circuits represented in Fig. 1, a summary of the manipulation of the switches necessary for the various measurements is given in Table I. To make a given measurement, the switches listed following that measurement should be closed and all others opened. The complexity of the set-up results largely from the fact that it is necessary to break the potentiometer measuring circuit simultaneously with the charge, and also with the discharge, for all measurements.

In order to provide a complete check on the results, it is necessary to measure the fall of potential over every portion of the

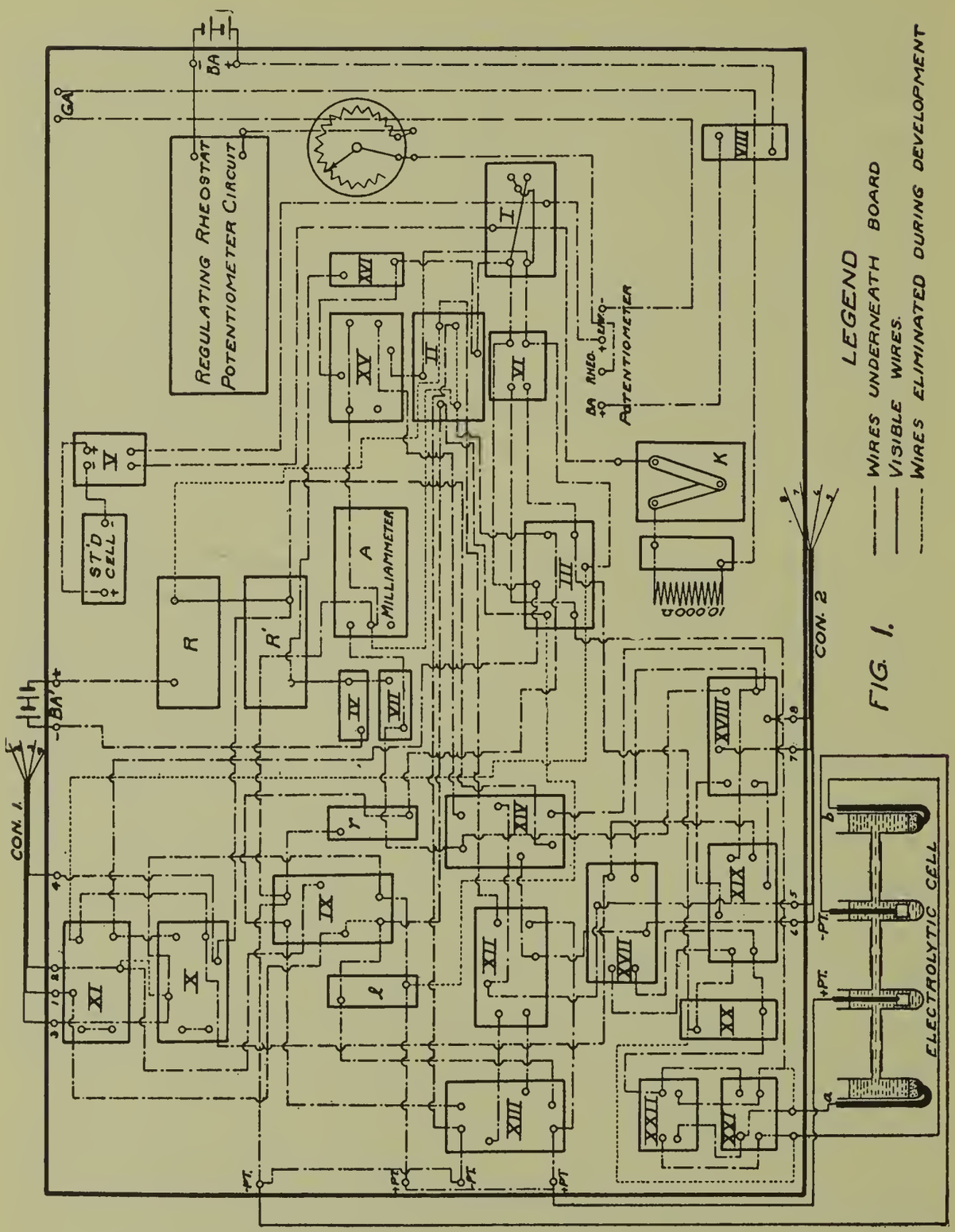

FIG. 1.

charging circuit. The fall of potential over the resistance R′, which is the source of the charging potential, must be found equal to the sum of, (1) the potentials delivered to the two electrodes, (2) the IR drop through the solution, (3) IR drop over brushes, (4) IR drop over ammeter, and (5) the IR drop over all the connecting wires. When this is the case, one may be certain that the apparatus is functioning properly.

Table I.

Switches Which Must Be Closed to Make the Potential Measurements Desired.

A. On charge with the interrupter stationary.
Switches XX and XXII closed.

Potentials to be measured	Switches
Charge	I, II (right), XII (right)
+Pt+HgO	I, III (left), XII (left), XIII (down)
—Pt—HgO	I, III (right), XII (right), XIII (up)
HgO—HgO	I, VI
Brushes	I, X (right)
Standard Resist.	I, XIV (up), XV (right)
Box R′	I, XIV (down), XVI

Switches XX and XXI closed.

+Pt—HgO	I, III (left), XII (left), XIII (down)
—Pt+HgO	I, III (right), XII (left), XIII (up)

B. On charge with the interrupter rotating.

Charge	I, II (right), XII (right), XXII, XX
+Pt+HgO	I, III (left), XII (left), XIII (down), XXII, XX
—Pt—HgO	I, III (right), XII (right), XIII (up), XXII, XX
HgO—HgO	I, VI, XII, XXII
Brushes	I, X (right), XVII (left), XXII
Standard Resist.	I, XV (right), XIV (up)
Box R′	I, XVI, XIV (down)
+Pt—HgO	I, III (left), XII (left), XIII (down), XX, XXI
—Pt+HgO	I, III (right), XII (left), XIII (up), XX, XXI

C. On discharge with interrupter rotating.

Discharge	I, II (left), IX (down), r
+Pt+HgO	I, III (left), IX (down), r, XX, XXII
—Pt—HgO	I, III (right), IX (up), XX, XXII
HgO—HgO	I, VI, XIII (left), XIX (left), XXII
Standard Resist.	I, XV (left), XVIII (right)
+Pt.—HgO	I, III (left), IX (down), r, XX, XXI
—Pt+HgO	I, III (right), IX (up), r, XX, XXI

An extensive series of measurements was made to test out every part of the set-up. The results were most satisfactory. The sum of the electrode potentials on charge and the fall of potential through the solution equalled the charge potential actually delivered to the cell. The sum of charge potential delivered to the cell, the fall over the brushes, the fall over the standard resistance, and the fall over the lead wires was just equal to the total charge potential or the potential across box R′. The sum of the

electrode potentials on discharge equalled the total discharge potential. The various measurements for the resistance of the solution all gave the same value.

The commutator (Fig. 2) consists of two discs mounted on one shaft. Each disc has two sets of brass and rubber sections; the brass plates on one set are exactly parallel to those on the other.

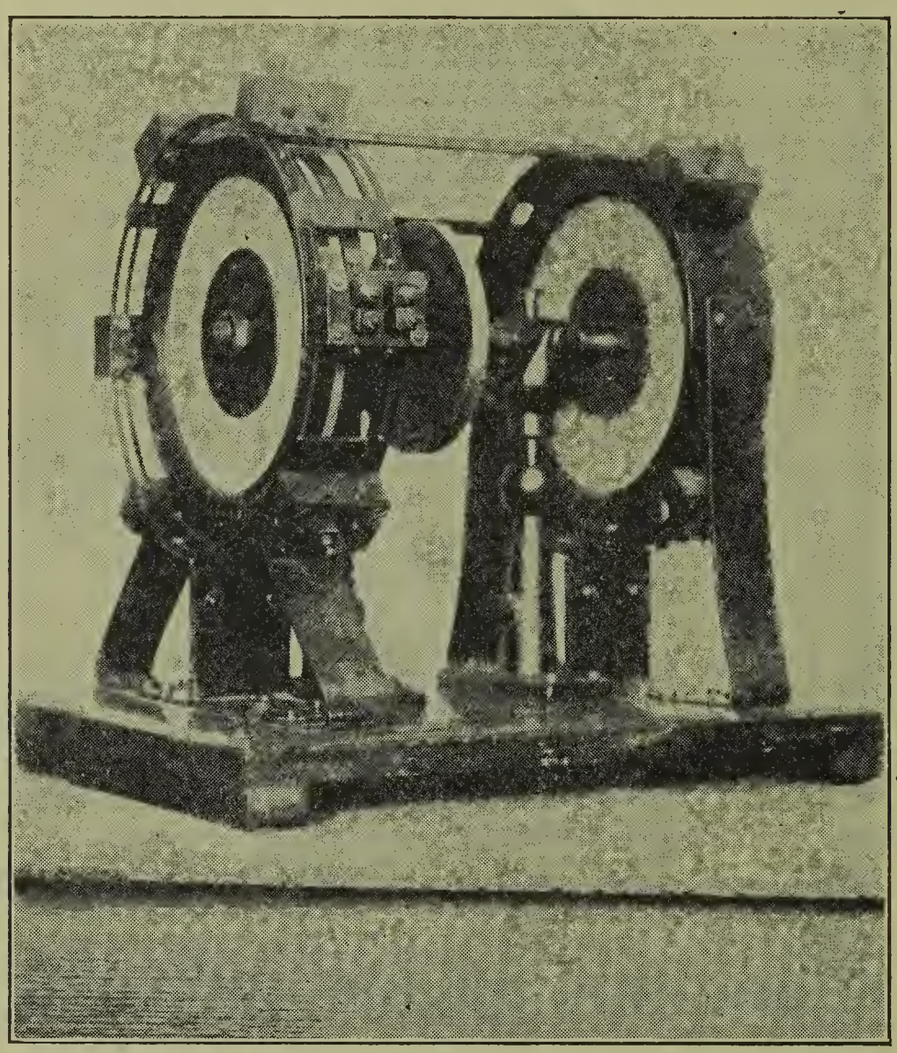

FIG. 2.

With this apparatus it is possible to measure decomposition potentials and overvoltages, by both the direct and commutator methods at the same time and under the same conditions. It was thought, however, that all of the measurements, although they check satisfactorily, might be in error due to the fact that the potentiometer was balanced first against the standard cell directly, and then against the unknown potential when one lead was broken

through the commutator, that is, there might be certain inductive effects introduced by the commutator.

To show that no error was introduced by this arrangement, the standard cell was first balanced in its usual position, and then when put in place of the electrolytic cell (with no current applied, of course). The measured value of the standard cell was found to be exactly the same as that used to obtain the original balance on the potentiometer, whether measured on charge or on discharge, when the interrupter was stationary. When the interrupter was started and the same measurements were made, the measured value was the same as before, both on charge and discharge, no matter what the speed of the interrupter.

All of the measurements up to this time showed that the potential of each electrode on charge was higher than the corresponding value on discharge, and also that the total charge potential was higher than the total discharge potential. This corresponds to what is generally reported in the literature, namely, that the direct method for measuring decomposition potentials gives higher values than the commutator method. Below the decomposition potential the difference is extremely slight, but it increases rapidly above this point.

The principal object of the present investigation is to obtain information which will account for the difference between the values obtained by these two methods. Those who favor the commutator method would probably say that it is due to the existence of a "transfer resistance" between the electrode surfaces and the electrolyte. The subject of "transfer resistance" will be discussed in another paper; it is sufficient to state here that the evidence obtained indicates that there is no such thing as "transfer resistance."

Several experiments were carried out to determine whether the relative sizes of the electrodes has an influence on the difference between the values obtained by the two methods. The solution used was in every case $N/1$ NaOH, and the reference electrodes Hg-HgO-$N/1$ NaOH. For lack of space the data are not included.

In one experiment, the anode, which was large, had a potential about 10 mili. v. higher on charge than on discharge at a current

of 27 mili. amp., while the cathode, which was small, had a potential 203 mili. v. higher on charge than on discharge for the same current (not current density). In another experiment the cathode, which was large, had a potential 11 mili. v. higher on charge than discharge, while the potential for the anode, which was small, was 170 mili. v. higher on charge than discharge at the same current, 30 mili. amp. In yet another experiment in which both electrodes were small and the same size, the cathode was 144 mili. v. higher on charge than on discharge; while the anode gave about the same difference as the cathode (150 mili. v.) between charge and discharge.

The results of this series of experiments show: (1) that the direct method gives higher values than the commutator method; (2) that the differences between the values by these two methods become greater the smaller the electrodes and the higher the applied potential; (3) that the potentials obtained by the commutator method are always higher on charge than on discharge and this difference becomes greater the smaller the electrode and the higher the current.

The important problem to be solved is, what is the cause for the difference between the potentials on charge and discharge? The remaining portion of this paper is an effort to solve this problem. This difference between the charge and discharge potentials might be due to one or more of three factors: (1) the presence of a constant resistance not so far accounted for; (2) the presence of "transfer resistance"; (3) the extremely rapid loss of polarization by the electrodes. The third factor is the only one considered at this time. The first and second factors are discussed in another paper on "transfer resistance."

If the difference is due to the decrease of polarization during the interval between the interruption of the charge potential and the measurement of the discharge potential, then by shortening this time the difference should become less. One method for reducing the time is to use the oscillograph, but this instrument requires too much current for experiments of this nature.

By a slight alteration of the commutator it became possible so to adjust the discharge brushes that the measurements on discharge were taken for only an exceedingly short time either just after the charge brushes left the brass plate or just before the

charge potential was again applied, or during the whole discharge interval. The difference between the first two values gave the loss in potential during a known period of time. It was thus possible to determine the rate of depolarization of the electrodes.

The time during which the value on discharge is measured may be calculated. Since there are three brass segments and three hard rubber segments, all of equal size, the length of time of each discharge interval is 1/r. p. m./60 x 1/6 sec., equals (10/r. p. m.) sec. If both discharge brushes are on the brass over only "d" degrees, then the time of each discharge is (10/r. p. m.) x d/60 sec. equals (d/6 r. p. m.) sec. The discharge value meas-

TABLE II.

Influence of Speed of Rotation of Commutator on Differences Between Electrode Potentials on Charge and Discharge.

Both electrodes small; about 6 mm. x 1 mm.

Series No.	r. p. m. (1)	I (2)	+Pt (3)	—Pt (4)
1	130	0.00125	0.034	0.0810
2	200	0.00125	0.023	0.0510
3	200	0.00105	0.019	0.0480
4	360	0.00105	0.006	0.0300
5	430	0.00107	0.004	0.0190
6	320	0.00179	0.025	0.0620
7	400	0.00178	0.021	0.0485
8	700	0.00177	0.015	0.0240
9	1350	0.00177	0.005	.....

ured is the average between the values at the time the discharge circuit is closed, and the time the discharge brushes leave the brass plate. The time interval which corresponds to the average potential measured is ½ of the total interval during which the potential on discharge is measured, or T equals ½ x d/6 r. p. m. equals (d/12 r. p. m.) sec. The two discharge brushes, also the two charge brushes, are on the brass at the same time for less than 60 degrees, since the distance between the brushes is about 4 degrees. This means that about 4 degrees are lost at one end of the brass segment.

It is evident from the above formula that T can be altered by varying either r. p. m. or d. If T is decreased by increasing

r. p. m., there should be a corresponding increase in the measured electrode potential, since the time allowed for self depolarization is decreased. This is shown to be the case by the results in Table II.

In Table II, column (1) gives the speed of rotation of the commutator, column (2) the current, column (3) the difference between charge and discharge at the anode, and column (4) the difference between charge and discharge at the cathode. The current and charge potential were constant for series 1 and 2; the same is true for series 3, 4 and 5, only the values are different; also for series 6, 7, 8 and 9.

TABLE III.

Influence of Length of Discharge Interval.

Anode (+Pt)		Discharge Interval in ° d	Cathode (—Pt)		r. p. m.
Charge	Discharge		Charge	Discharge	
.....	....	40	1.8010	1.790	400
1.122	1.1100	32	1.8010	1.800	400
1.122	1.1170	23	1.8015	1.803	400
1.123	1.1225	14	1.8010	1.809	400
1.123	1.1270	7	1.8020	1.819	400

The results in Table II show that at constant current the difference between the potentials of an electrode on charge and discharge (column 3 and 4) decrease with increase in the speed of rotation of the commutator.

It is possible to change the interval over which the discharge potential is measured by shifting the positions of the brushes. In one position the potential measured is an average discharge potential over a short interval, just after the applied potential is interrupted. This average value increases as r. p. m. is increased. Likewise the average potential of the electrode over a short interval, just before the potential is again applied, is measured by adjusting the brushes to another position. This average value also increases as r. p. m. is increased.

Since the values obtained under the first condition are for the first part of the discharge period, and those obtained under the

second condition are for the last portion of the discharge period, the former should be higher than the latter, and their average should be approximately equal to the values obtained under the condition where the measured value is for the whole period. This last statement is only approximately true, since the rate of self-depolarization is not the same over the whole period. The experiments carried out showed that the statements just made are entirely correct.

The results for one short experiment which is typical of the many performed at this time are included in Table III.

The results in this table show that as the value of d decreases the values for the potentials of the anode (+Pt) and cathode (—Pt) on discharge approach, become equal to, and at small values for d exceed their values on charge. The values measured on charge, over 56° of the plate do not change appreciably. As the length of the interval during which the electrodes discharge is shortened, it is to be expected that their potentials should approach and finally become equal to their values on charge; but it is certain that their discharge values can never exceed their true charge values. This indicates that the measured values on charge are too low. The next experiment is an investigation of the potentials on charge.

When the potential of an electrode is measured on charge and the applied potential is suddenly interrupted the potential of the electrode drops several tenths of a volt in one second or less. If the potential is again applied, the electrode does not immediately come to its former value, but several seconds and often even minutes are required. Although the time during which the applied potential is interrupted, when the commutator is in motion, is very short, it seems plausible to assume that the electrode does not come to its full charge value instantaneously when the charge is again applied. It seems probable, therefore, that the measured potential of the electrode is an average between the value it has at the first instant that the potential is applied and the value it has just before the applied potential is interrupted.

The time interval which corresponds to the measured average value is calculated by the formula given above. The average potential applied, during any definite portion of the charge interval, is measured by a proper location of the measuring brushes.

If the brushes in the charging circuit and the brushes which break the potentiometer circuit simultaneously with the charge are in their regular positions, the measured value is the average potential of the electrode on charge over 56°, or practically the whole length of a brass plate. Experiments were carried out in which measurements were made with the charge brushes adjusted to different positions.

The results show that the average values on charge over the last part of the plate are higher than the average values over the whole plate (56°); also, that the average values over the first part of the plate are lower than over the whole plate. The sum of the average value over a certain portion of the first part of the plate, and the average value over an equal portion of the last part, divided by two equals approximately the measured average value over the whole plate. It is evident from these results, that after an electrode has reached such a potential that it loses its charge rapidly, the values measured are in all cases averages. This statement holds true especially for small electrodes or for large electrodes at high current densities.

The values for the electrode potentials over the shortest interval, for the first part of the plate, are the lowest obtained, because the charge potential has just been applied; but as the interval becomes larger the potentials increase, and then, as the shift is made to the last part of the plate the potentials continue to increase as the interval over which they are measured decreases, and reach a maximum at the smallest interval, because here the charge potential has been applied for the longest period; but even here the potential is still less than that obtained by the direct method, that is with the interrupter shorted. *This means that the commutator method can probably never give values for charge potentials which are the same as those obtained by the direct method.* It also means that values for charge potentials obtained by the direct method cannot be used in connection with discharge values obtained by the interrupter method. Just this thing has, however, been done by previous investigators in their calculations of "transfer resistance," and is probably the main cause for the apparent existence of such a "resistance."

The values measured over the last part of the plate on charge, and over the first part of the plate on discharge, become more

nearly equal the smaller the values for d and the more rapid the commutator rotation. In all of these experiments, the values of the electrode potentials measured at the beginning of the discharge interval were greater than the values at the beginning of the charge.

The experiments also show that even the measured current values are averages. When a cell with a low definite potential is interrupted for even a short time, the potentials of the electrodes decrease. If the potential is again applied, the current is higher at first, and then decreases as the potentials of the electrodes increase. The same thing happens when the interrupter is rotating, though of course the time interval during which the applied potential is interrupted is very short.

In order to confirm the various statements which have been made, several series of experiments were carried out, in which practically every type of measurement made in the previous work is included. The measurements in each set of experiments were made under the same conditions and are therefore comparable. For lack of space, only about the last third of the results of only one such experiment is included in this paper (Table IV). In this experiment two small electrodes were used.

In every series of readings thirty-seven potential measurements were made in rapid succession after the applied potential had become constant. The measurements in section 1 of the table include the potentials on charge with the interrupter shorted; section 2, those on charge and discharge over 56° of the plates; section 3, those over the last 15°, and section 4, those over the first 15°. The measurements were made in this order. The order of measurements in each section is indicated by the column numbers.

The results in these tables confirm in every respect conclusions drawn from previous tables. In each section the sum of the electrode potentials (columns 2 and 3) on charge, and the IR drop through the solution (column 6), equals the applied potential (column 1), and the sum of the potentials of the electrodes on discharge (columns 9 and 10) equals the discharge potential (column 8). The values for the IR drop through the solution, obtained by subtracting the electrode potentials (2 and 3) from the corresponding values obtained by measuring the potential of

TABLE IV.—*Summary Table. Small Electrodes.*

SECTION 1—Interrupter Stationary. Potentials Are Those Obtained by the Direct Method.

Series No.	Time	Ratio R'-R	Time	Charge (1)	+Pt +HgO (2)	—Pt —HgO (3)	+Pt —HgO (4)	—Pt +HgO (5)	HgO —HgO (6)	I (7)	Cell R (11)
	12/19/22										
1	*11:25	750-900	11:50	2.2350	1.0558	1.0988	1.1362	1.1790	0.0800	0.0010052	79.59
2	*12:15	900-900	2:20	2.3100	1.0776	1.1322	1.1780	1.2326	0.1002	0.001340	74.78
3	*2:55	1000-600	3:35	2.5030	1.1120	1.1886	1.3136	1.3901	0.2012	0.002749	73.19
4	*5:15	1000-400	6:05	2.7095	1.1483	1.2522	1.4578	1.5615	0.3095	0.004245	72.92
6	*9:45	1000-200	10:38	3.1380	1.2245	1.3670	1.7724	1.9150	0.5475	0.007230	75.72
	12/20/22										
7	*11:15	1000-100	9:40 A.M.	3.7246	1.3192	1.6990	2.0250	2.4056	0.7055	0.009389	75.14

SECTION 2—Interrupter Rotating, Potentials Measured Over Whole Plate by Commutator Method

Series No.	Time	Charge (1)	+Pt +HgO (2)	—Pt —HgO (3)	+Pt —HgO (4)	—Pt +HgO (5)	HgO —HgO (6)	I (7)	Discharge (8)	+Pt +HgO (9)	—Pt —HgO (10)	Cell R (11)
1	11:55	2.1942	1.0361	1.0724	1.1217	1.1581	0.0861	0.001130	2.0865	1.0245	1.0614	76.20
2	2:30	2.2610	1.0550	1.0987	1.1614	1.2055	0.1065	0.001425	2.1242	1.0400	1.0847	74.74
3	3:45	2.4524	1.0910	1.1518	1.2995	1.3597	0.2085	0.002852	2.1776	1.0572	1.1205	73.11
4	6:08	2.6450	1.1260	1.2010	1.4452	1.5290	0.3190	0.004377	2.2300	1.0732	1.1562	72.86
5	9:15	2.7000	1.1434	1.2415	1.4565	1.5545	0.3130	0.004265	2.2735	1.0890	1.1842	73.39
6	10:45	3.1000	1.2025	1.3363	1.7630	1.8965	0.5605	0.007357	2.3548	1.1180	1.2347	76.19
	12/20/22											
7	9:50	3.6700	1.2835	1.6635	2.0054	2.3850	0.7220	0.009612	2.6460	1.1655	1.4795	75.11
8	11:05	3.6690	1.2795	1.6766	.....	.....	0.7120	0.009623	2.6670	1.1655	1.4990	74.00

SECTION 3—Interrupter Rotating, Measurement Made Over the Last 15° ±1, Commutator Method

Series No.	Time	Charge (1)	+Pt +HgO (2)	−Pt −HgO (3)	+Pt −HgO (4)	−Pt +HgO (5)	HgO −HgO (6)	I (7)	Discharge (8)	+Pt +HgO (9)	−Pt −HgO (10)	Cell R (11)
	12/19/22											
1	12:01	2.2101	1.0466	1.0807	1.1297	1.1637	0.0837	0.001097	2.0687	1.0135	1.0548	76.30
2	2:37	2.2812	1.0673	1.1095	1.1708	1.2132	0.1040	0.001390	2.1010	1.0267	1.0740	74.81
3	3:53	2.4800	1.1058	1.1696	1.3095	1.3735	0.2040	0.002791	2.1435	1.0402	1.1030	73.09
4	6:15	2.6880	1.1425	1.2350	1.4550	1.5475	0.3130	0.004284	2.1840	1.0535	1.1306	73.06
5	9:20	2.7364	1.1593	1.2702	1.4652	1.5760	0.3064	0.004166	2.2242	1.0680	1.1560	73.55
6	10:55	3.1380	1.2210	1.3655	1.7730	1.9180	0.5540	0.007201	2.2940	1.0930	1.2002	76.93
	12/20/22											
7	10:05	3.7016	1.2980	1.6930	2.0070	2.4016	0.7082	0.009452	2.5602	1.1335	1.4270	74.93
8	11:15	3.7000	1.2950	1.7055	.....	.....	0.6970	0.009450	2.5760	1.1335	1.4415	73.76

SECTION 4—Interrupter Rotating, Potentials Measured Over the First 15°, Commutator Method

1	12:07	2.1730	1.0212	1.0630	1.1098	1.1522	0.0886	0.001172	2.1096	1.0375	1.0720	75.60
2	2:45	2.2310	1.0366	1.0843	1.1467	1.1940	0.1100	0.001481	2.1529	1.0550	1.0970	74.27
3	4:00	2.4026	1.0625	1.1240	1.2775	1.3395	0.2145	0.002952	2.2265	1.0808	1.1456	72.66
4	6:23	2.5870	1.0890	1.1660	1.4210	1.4970	0.3032	0.004555	2.2905	1.1005	1.1895	66.56
5	9:30	2.6244	1.1040	1.1930	1.4305	1.5205	0.3268	0.004455	2.3410	1.1175	1.2224	73.35
6	11:05	3.0240	1.1610	1.2750	1.7495	1.8640	0.5888	0.007626	2.4430	1.1565	1.2860	77.21
7	10:15	3.5570	1.2280	1.5665	1.9900	2.3272	0.7620	0.010202	2.7700	1.2080	1.5595	74.70
8	11:20	3.5570	1.2255	1.5810	.....	.....	0.7510	0.010190	2.7770	1.2060	1.5740	73.70

each electrode against the opposite standard, and thus including the IR drop through the solution (columns 4 and 5), agree well with the values of the IR drop obtained by measuring the potential between the two standard electrodes (column 6).

Before one of these experiments (the data for which are not recorded in this paper) was performed, the resistance of the cell was determined by the Kohlrausch method, and was found to be 78.2 ohms. After the experiment the resistance was again determined, and found to be 80.1 ohms. The resistance calculated from any of the values for the IR drop through the solution was the same, within the limits of experimental error as the value by the Kohlrausch method.

The tables also show that in each series all of the values measured over 56° (section 2) of the plate, are approximately the averages of those in sections 3 and 4. Even the resistance of the cell as calculated in 2, 3 and 4 makes it appear that the values in 2 are the averages of those in 3 and 4.

CONCLUSIONS.

The conclusions to be drawn from this work are: (1) The absolute values obtained by the commutator method are practically meaningless, since they depend upon the mechanical construction and operation of the commutator. (2) There is a decided indication that the commutator and direct methods would give the same measured values if the measurements by the commutator method could be made at the instant the charging circuit is interrupted. Further work is now in progress along this line.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 25, 1924, Mr. S. Skowronski in the Chair.

METAL CLEANSING WITH ALKALINE CLEANING SOLUTIONS.[1]

By E. M. Baker and Richard Schneidewind.[2]

Abstract.

The efficiency of alkaline cleaning solutions may be judged from measurements of the relative interfacial tensions of water and these solutions with a standard mineral oil. Measurements have been made of these interfacial tensions for solutions of many substances ordinarily found in commercial cleaners. These measurements indicate soaps, NaOH, Na_3PO_4, Na_2CO_3 and sodium silicates to be the most effective components of alkaline cleaners. Typical analyses are given of cleaners used for various purposes, and factors entering into the mixing of cleaners are discussed.

The success of many processes such as electroplating and japanning is in a great measure dependent upon properly preparing the surface of the metal to be so treated. This entails the removal of all "foreign matter" and the production of a perfectly clean, grease and oil-free surface. There are several kinds of foreign matter, and these may be conveniently classified into three groups:

1. Oxides, such as rust and scale on steel, which result from exposure or from heating operations.
2. Grit, such as emery dust.
3. Oil and grease, which result from various machining, or slushing operations.

Rust, scale, and other oxides are best removed by pickling, either with or without the use of electric current. For some

[1] Manuscript received February 1, 1924.

[2] Contribution from the Dept. of Chemical Engineering, University of Michigan, Ann Arbor, Mich.

classes of work sand blasting has been successful, because this treatment produces an ideal velvety surface for plating or japanning. Alkaline cleaners are not effective in removing this type of foreign material.

Grit and oil, for grit is always held on by means of oil, are removed simultaneously. For this purpose, three general methods are in use.

1. *The "Burning off" Process.* The work is placed in ovens and heated to about 232° C. (450°F.) for 15 to 20 min. The oil and grease are thus largely removed by volatilization and carbonization, and the grit, if present, is no longer adherent and falls off, or may be removed by an air blast or by tack ragging. This process is satisfactory preparatory to japanning, but is not suitable for work to be plated. One inherent defect is the tendency to form a light coat of oxide on the metal.

2. *Organic Solvents.* The work is washed, with or without brushing, in a tank. The solvent dissolves the oil or grease and the agitation removes the grit. Kerosene, gasoline, spirit naphtha, benzol, and dichlorbenzol are typical of the solvents used. Often the pieces are subsequently tumbled in sawdust to dry them. The quality of cleaning done by this process is high, but the objections which may be raised against it are gradually making this method less favored wherever there is a large volume of work to be done. The fire hazard is great, the fumes are decidedly unpleasant to the operator, and the evaporation losses are large. Also the solvent soon becomes contaminated with oil. The cost of organic solvents as compared with alkaline metal cleaners is high, and in fact is prohibitive unless an efficient recovery system is installed.

3. *Alkaline Metal Cleaners.* These are aqueous solutions containing such substances as sodium hydroxide, carbonate, tribasic phosphate, borate, silicate, sulfate and soaps. They may be used in various ways such as in:

a. Steel tanks, in which the work is simply immersed in solution kept hot by means of steam coils.

b. Electrocleaning tanks, in which the hot solution forms the electrolyte, and the tank and work serve as anode and cathode, or *vice versa.*

c. Machines, in which the work is carried along on an endless conveyor, over which hot solution is either splashed or poured.

The concentration of solutions used for electrocleaning is usually lower than the concentration of solutions used for other methods, but if the temperature of all solutions is kept high the only advantage ordinarily claimed for the use of electric current is speed of cleansing.

Although the number of commercial cleaning compositions is large, the great majority of cleaners may be grouped into a few general classes:

I. *Enamel Removers.* Analyses of over fifteen so-called "enamel removers," which is the designation of compositions for "very heavy duty" cleaning, and for stripping japan, show approximately the following formula: NaOH, 85 per cent; Na_2CO_3, 10 per cent; rosin, 5 per cent. This is a very effective mixture. The caustic, together with the rosin soap which is formed, is most effective in cleaning, the carbonate aiding but little and being added presumably because it is traditional to do so. Actual shop tests by the junior author show the addition of carbonate both unnecessary and without noticeable effect.

II. *Heavy Duty Cleaners.* For ordinary "heavy duty" cleaning such as removing quenching oil, and for service where a thoroughly clean surface is not needed, a different type of mixture is used. The composite analysis of representative compositions of this class is approximately: NaOH, 35 per cent; Na_2CO_3, 57 per cent; rosin, 8 per cent.

For a still milder action, a cleaner composed of 90 per cent Na_2CO_3 and 10 per cent rosin may be used. These cleaners are not as free rinsing as the class immediately following, but may be used as plater's cleaners if especial care is taken to rinse thoroughly.

III. *Rapid Rinsing or Plater's Cleaners.* For cleaning metal preparatory to plating, rapid rinsing as well as rapid thorough cleaning is imperative. The analyses of over 20 compositions used for this purpose showed: $Na_3PO_4 . 12H_2O$, 50-70 per cent; Na_2CO_3, 40-20 per cent; NaOH, 10 per cent; soap, optional up to 4 per cent of the mixture.

IV. *Light Duty Cleaners.* For all around "light duty" cleansing, such as laundry and janitor work, and for cleaning non-ferrous metals, most of the compositions contain a high percentage of tribasic sodium phosphate, with additions of sodium carbonate or borate.

V. *Miscellaneous Cleaners.* There are various "special purpose" cleaners. An example of one of these is the following aluminum cleaner: NaOH, 6 per cent; Na_2CO_3, 56 per cent; $NaAlO_2$, 8 per cent; Na_3PO_4, 30 per cent.

This is a fused product ground for the trade. Ordinary aluminum castings which contain small percentages of copper will turn black in solutions of so weak an alkali as trisodium phosphate, but will not tarnish even through protracted boiling in solutions of compositions similar to the above. Thus sodium aluminate appears to protect aluminum-copper castings from tarnishing, when these are boiled in alkaline solutions. The following analysis is typical of another special cleaner, which contains suspended material, and is used for general cleaning: NaOH, 42 per cent; Na_2CO_3, 3 per cent; Na_2SiO_3, 18 per cent; insoluble, 12 per cent; water, 25 per cent.

Little theoretical work has been published on the subject of metal cleansing by alkaline solutions. Extravagant claims for their products are not uncommonly put forward by makers of commercial compositions. Shop tests are generally used as a basis in selecting cleaners for various purposes. There is, however, no accurate criterion for judging the quality of cleansing obtained, unless there is a marked difference in the effectiveness of the cleaners. Ordinarily the difference is minor, if the cleaners are similar in composition and concentration.

The personal factor in judging the results of the shop test enters largely, and the authors have seen a number of instances where two cleaners, identical in composition and operating under nearly identical conditions on the same batch of work, have been judged to give greatly different results. Many makers and users of cleaners have little faith in chemical analysis of these products, claiming either that cleaners cannot be analyzed, or that the analysis is no criterion of the performance. Thus one cleaning composition which is only a mixture of two salts, each costing around

4 cents per pound sells for 12 to 15 cents per pound, while the identical mixture, compounded by another maker, must go begging at a price of 10 cents per pound.

A study of the literature on the subject indicates that investigators are in substantial agreement in ascribing the effectiveness of alkaline cleaning solutions to the power of these solutions to form emulsions with oil. As early as 1899, Donnan[3] recognized that the cleansing power of a substance was proportional to its power of emulsification with the substance to be removed. Hillyer,[4] described measurements with a Traube stalagmometer on the interfacial tensions of sodium hydroxide solutions and olive oil. Unfortunately since the oil to be removed is generally unsaponifiable mineral oil, rather than animal or vegetable oil, these data are not directly applicable to metal cleansing. V. Lehner and M.V.R. Buell[5] used a similar apparatus in experimenting with soaps and oils such as kerosene, benzol, tuluol and cottonseed oil. H. G. Elledge and J. J. Isherwood[6] used Hillyer's apparatus with kerosene and alkaline solutions. They report that if solutions of NaOH, Na_2CO_3 or $Na_3PO_4 . 12H_2O$ in equimolecular concentrations up to 1 gram per liter are used, these substances are equally effective. They state also that solutions of NaOH, Na_2CO_3 and $Na_3PO_4 . 12H_2O$ showed little change in emulsifying effect with changing concentration. Elledge and Isherwood used kerosene; and with an oil of so low a viscosity the differences in behavior of dilute alkaline solutions under varying conditions of concentration are so slight that they cannot readily be determined. Use of a more viscous oil would have resulted in different conclusions.

While the emulsifying power with oil is of prime importance in determining the effectiveness of the solution, there are other factors which are sufficiently important to warrant attention. We consider the more important factors to be solution of metallic oxides, saponification of fats, and adsorption and emulsification phenomena. The first two of these are chemical effects; the latter two are physical effects.

[3] Z. phys. Chemie, **31**, 42 (1899).
[4] J. Am. Chem. Soc., **91**, 200 (1907).
[5] J. Ind. Eng. Chem., 8, 701-3 (1916).
[6] J. Ind. Eng. Chem., 8, 793-4 (1916).

I. *Solution.* Alkaline substances, notably cyanides, exert a slight solvent effect on metallic oxides, according to Scott[7] and Pradel.[8] Cyanide is widely used to remove tarnish from jewelry, but has not found favor as a component of alkaline cleaners.

II. *Saponification.* When the oil is of animal or vegetable origin, the alkali slowly reacts with it, slightly saponifying it and thus rendering it partially water soluble. Hillyer's work on NaOH and cottonseed oil really showed the effect from an emulsification standpoint, of NaOH plus some sodium oleate soap formed in the experiment. The removal of grease and oil by saponification represents a distinctly special case of cleaning.

III. *Adsorption.* Some substances, presumably through bubbles formed by agitation of the solution, will adsorb and remove from the work, small particles of adherent material, which may be designated as grit. One of the best agents for this purpose is soap. Sodium silicate solutions also exhibit this tendency to a lesser extent.

IV. *Emulsification.* A review[9] and discussion of the theories of emulsification is not within the scope of this paper. The investigations of emulsions have largely been directed toward the production or breaking of permanent emulsions. The emulsions produced in metal cleansing are ordinarily not permanent emulsions, but rather are unstable emulsions, forming at the surface of the work to be cleansed, and soon breaking down and allowing the oil to come to the surface of the solution. With emulsions of this type, formed from solutions used in metal cleansing, the authors believe that the emulsifying power of the solution is dependent on the lowering of the interfacial tension between the grease or oil and the solution, by the dissolved substance or substances, and that a measure of this lowering of interfacial tension is a measure of the effectiveness of the dissolved substance or substances used as cleansing agents.

This lowering of interfacial tension is illustrated in a non-technical way by a simple experiment, which will be described by

[7] Metal Ind. n.s., 12, 467 (1914).

[8] Elektrochem. Z., 16, 215-46.

[9] L. W. Parsons, J. Ind. Eng. Chem., 14, 797 (1922) gives references to a number of summaries of the literature of emulsions.

reference to the illustrations of Fig. 1. Water, alkaline metal cleaner, and petroleum ether are represented as issuing slowly from a capillary tube immersed under mineral oil. From tube A the water emerges as a drop of definite size, the size of the drop depending in part on the viscosity of the oil as will be shown later. From tube C, the petroleum ether on emerging goes almost immediately into solution and no drops are formed. From Tube B the solution emerges as a drop smaller than the drop of water from the tube A. The drop of solution is also of definite size, depend-

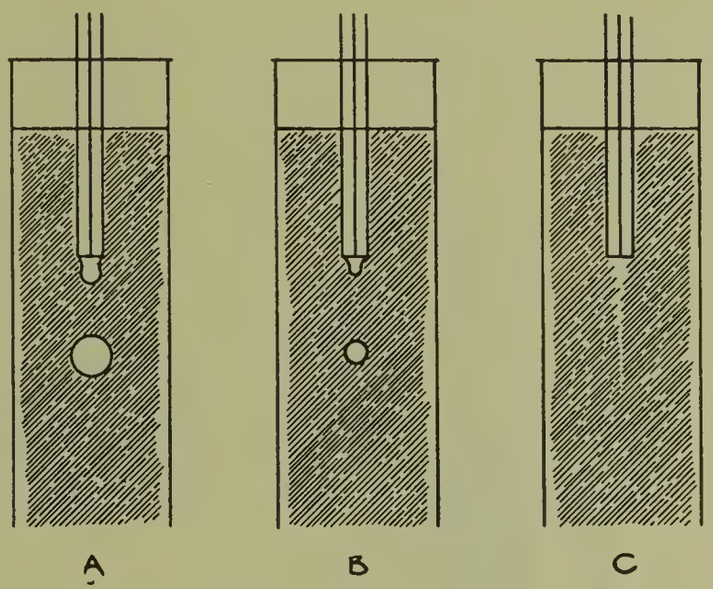

FIG. 1. Illustration of effect of interfacial tension on the size of drop formed when one liquid issues from a capillary tip into another liquid.

Tube A represents water entering oil. The interfacial tension is large and the drop formed is large.

Tube B represents a solution of alkaline metal cleaner entering oil. The interfacial tension is less than that between water and oil, and the drop is smaller than that formed from Tube A.

Tube C represents petroleum ether entering oil. The interfacial tension is zero, the petroleum ether goes into solution with the oil, and no drops are formed.

ing primarily on the viscosity of the oil, and on the concentration and nature of the substances dissolved in the water.

An apparatus similar in principle to a Traube stalagmometer was devised to measure, under similar standard conditions, the relative surface tensions of systems of water and a definite mineral oil, and of solutions of alkaline salts with the same oil. This was accomplished by comparing the size of drops of aqueous alkaline solutions, issuing from a capillary tube beneath the surface of oil, to the size of drops formed in the same manner by distilled water. A drawing to scale of this apparatus is shown in Fig. 2.

In Fig. 2, (1) is a Shellbach burette, provided with a ground surfaced tip of 5.7 mm. outside diameter, with a hole 0.31 mm. in diameter. In order to insure proper heating of the solution in the burette before issuing from the orifice, the tip was always kept 7 cm. below the heated oil in the receiver (2). The receiver was a glass cylinder 3 cm. in diameter, 18 cm. long, and sealed at the bottom to a small tube (3) which connected with a suction pump. This tube functioned as a discharging device for the aqueous solution, which sank to the bottom of the receiver. Four

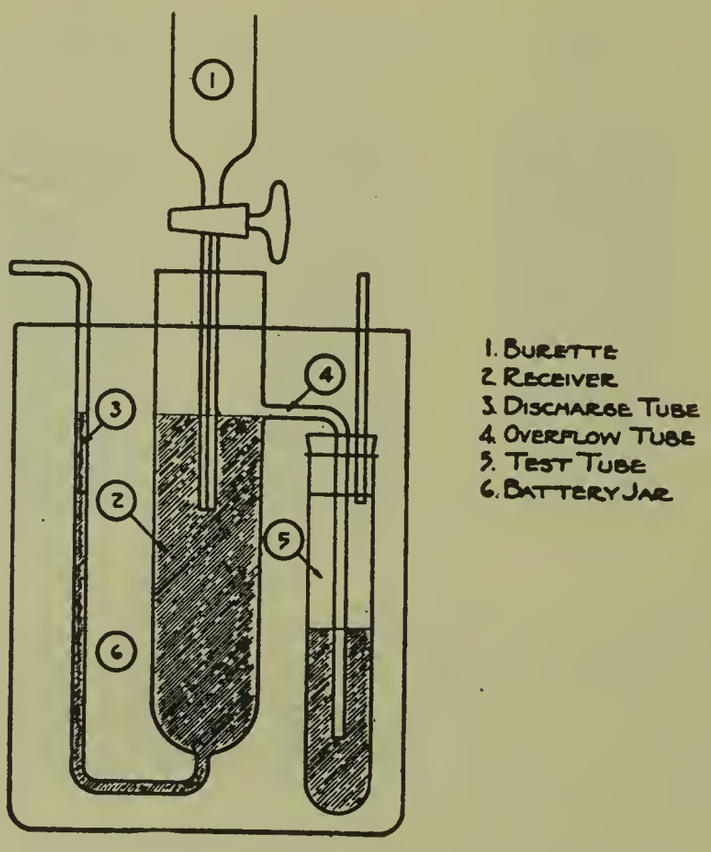

Fig. 2. Elevation view of apparatus used in determining comparative drop size of various solutions.

cm. from the top of the receiver another tube (4) was attached, which acted as an overflow in order to maintain a constant level of oil within the apparatus. The overflow oil was caught in a test tube (5) fitted with a two-holed rubber stopper, one hole of which admitted tube (4). Through the other hole passed a glass tube, by means of which the oil could be blown back to the receiver.

The receiver and the overflow oil reservoir were placed in a water jacket, consisting of a battery jar (6), 8 cm. by 20 cm. by 25 cm. high. The water was electrically heated by means of

resistance wire stretched over insulated posts in the corners of the jar. The temperature of the water and therefore of the oil in the receiver could be regulated by means of a rheostat, in series with the heating coil. Some oil was poured on the surface of the water to prevent evaporation.

For illumination a 40-watt Mazda B lamp, with a reflector, was placed behind the battery jar. A sheet of paper was placed over the front of the reflector to diffuse the light.

The oil used in all of this experimental work was Gargoyle Mobiloil E, which is quite representative of the usual mineral oil encountered in practice. Furthermore it is a clear oil of a viscosity satisfactory for experimental purposes, and is sufficiently uniform to permit duplication of results.

The oil in the reservoir was brought to the desired temperature. The burette containing the solution, the surface tension of which was to be tested, was then lowered so that the tip was a definite distance below the surface of the oil. Then the solution was allowed to drop from the tip at a uniform rate. The volume of a definite number of drops was read from the burette. This divided by the volume of the same number of drops of distilled water gives the "drop ratio," or "comparative drop size."

Some difficulties were experienced in measuring the relative drop sizes. This necessitated the adoption of standard procedures. If dropping was too rapid, each large drop would break off from the tip and carry in its wake a smaller "sister drop." A photograph of a large drop followed by such a "sister drop" is shown in Fig. 3a, while a photograph of a normal drop, formed by flowing the solution only slightly slower from the tip, is shown in Fig. 3b. In these determinations dropping was effected at the maximum speed that could be maintained without the formation of these sister drops.

When working with highly effective cleaning solutions, the oil would soon become contaminated with small amounts of emulsions, and the data would not be uniform. As soon as the oil became the least bit turbid, it was rejected. Contamination of the oil could readily be detected by determining the drop size with distilled water. A smaller drop size of water indicated contamination of the oil. A check run of distilled water was made after every fifteen readings.

It was impossible to determine values for the relative interfacial tensions for solutions of sodium hydroxide having a concentration higher than 8.2 g. of NaOH per L. The drops formed in these cases were so small that they would not spread out over the entire ground tip. Instead they formed almost within the capillary itself, and no reliable readings could be taken.

FIG. 3a FIG. 3b

FIG. 3. Photographs of normal drop and drop followed by smaller sister drop formed by a solution of alkaline cleaner issuing under oil.

FIG. 3a. Shows the effect of running the solution too rapidly from the capillary tip, resulting in one or more small sister drops following the normal drop.

FIG. 3b. Shows the normal drop formed by running the solution from the tip at the correct rate.

It was deemed advisable first to investigate alkaline solutions containing only a single dissolved substance, and to test these solutions all at one temperature and with a mineral oil of known viscosity. Solutions of a few binary mixtures of some of the common salts were also tested. Measurements were subsequently made with some solutions of a single substance, using the same oil at different temperatures and similar oils of various viscosities at

the same temperature. It was found possible to correlate all results.

Stock solutions of substances to be tested were made up containing 90 g. of solute per L. of solution (12 oz. per gal.) This concentration is higher than is ever found in practice. Less concentrated solutions were formed by diluting these stock solutions. The substances investigated were NaOH, Na_2CO_3, $Na_3PO_4 . 12H_2O$, $Na_2HPO_4 . 12H_2O$, $NaHCO_3$, $Na_2B_4O_7 . 10H_2O$, $Na_2SO_4 . 10H_2O$, $NaHSO_4$, sodium silicate, gelatine and soaps. The sodium silicate was 60° Be. (1.7 sp. gr.) commercial water glass, diluted to give a stock solution containing 75 g. per L. of salt figured as Na_2SiO_3 from the SiO_2 content. The soaps used were ivory and castile. The gelatine was a pure colorless substance sold for biological purposes. The other substances were C. P. reagents.

For the sake of brevity the results are presented in tables and graphs.

Table I, and Fig. 4, 5, and 6 contain the data obtained from solutions of single substances and Mobiloil E at 83° C. Fig. 4 shows that for any given normality of dissolved substances sodium hydroxide, tri-sodium phosphate, sodium carbonate, and sodium silicate are far more effective in lowering the comparative drop size, than are solutions of other substances on which data are presented in this figure. Likewise, sodium hydroxide, a strong alkali, and trisodium phosphate, a weakly alkaline salt, are nearly equally effective if used in concentrations of equal normality, and are superior to sodium carbonate and silicate as well as the less effective salts. $NaHSO_4$, an acid salt, is almost as effective as the neutral salt, Na_2SO_4. Fig. 4 shows further that the comparative drop size is decreased rapidly with increasing concentrations of solutions up to 0.1 normal, after which the effect of increasing concentration falls off appreciably, until at 1 normal the comparative drop size has become practically constant.

Fig. 5 and 6 present curves that lead to the same conclusions as the curves of Fig. 4. The concentrations of solutions are given in weight units per volume of solution, and are therefore useful in computing the cost of a solution which will produce a given lowering of comparative drop size. Gram for gram, sodium hydroxide is much more effective than the other substances. Tri-

TABLE I.

Relative drop size of solutions of single substances.

Temperature 83° C. Checked against distilled H_2O. Each value is the average of at least three concordant values.

Material	Concentration			Comparative Drop Size
	g./L.	oz./gal.	Normality	
1 Glauber salt, $Na_2SO_4.10H_2O$	90	12	0.560	0.79
	60	8	0.373	0.83
	45	6	0.279	0.85
	30	4	0.186	0.90
	15	2	0.093	0.95
	7.5	1	0.046	0.99
2 Sodium Bicarbonate, $NaHCO_3$	90	12	2.14	0.55
	60	8	1.43	0.62
	45	6	1.07	0.68
	30	4	0.713	0.72
	15	2	0.357	0.76
	7.5	1	0.179	0.78
3 Water Glass, 60° Be., Na_2SiO_3	37.4	4.99	0.614	0.21
	24.9	3.22	0.410	0.29
	18.7	2.49	0.307	0.33
	12.5	1.66	0.154	0.37
	6.23	0.83	0.103	0.49
	3.40	0.45	0.051	0.56
4 Dibasic Sodium Phosphate, $Na_2HPO_4.12H_2O$	90	12	0.752	0.63
	60	8	0.502	0.69
	45	6	0.375	0.77
	30	4	0.251	0.83
	15	2	0.125	0.91
5 Soda Ash, Na_2CO_3	90	12	1.70	0.12
	60	8	1.13	0.16
	45	6	0.850	0.18
	30	4	0.565	0.21
	15	2	0.283	0.30
	8.17	1.09	0.154	0.36
	6.67	0.89	0.126	0.42
	5.11	0.68	0.0959	0.47
	3.48	0.46	0.0653	0.52
	1.77	0.24	0.0333	0.61
6 Niter Cake, $NaHSO_4$	85	11.3	1.42	0.67
	56.7	7.55	0.945	0.72
	42.5	5.65	0.708	0.76
	28.3	3.77	0.475	0.82

TABLE I—Continued.

Relative drop size of solutions of single substances.

Material	Concentration			Comparative Drop Size
	g./L.	oz./gal.	Normality	
7 Borax, $Na_2B_4O_7.10H_2O$	90	12	0.471	0.53
	60	8	0.314	0.61
	45	6	0.236	0.66
	30	4	0.157	0.70
	15	2	0.0784	0.79
8 Tribasic Sodium Phosphate, $Na_3PO_4.12H_2O$	90	12	0.710	0.064
	60	8	0.473	0.12
	45	6	0.355	0.14
	30	4	0.237	0.17
	15	2	0.118	0.26
	8.17	1.09	0.065	0.36
	7.50	1.00	0.059	0.38
	6.67	0.89	0.053	0.41
	5.11	0.68	0.040	0.46
	3.48	0.46	0.027	0.52
	1.77	0.24	0.014	0.65
	0.89	0.12	0.007	0.70
9 Caustic Soda, NaOH (Not determinable at higher concentrations.)	8.17	1.09	0.204	0.17
	6.67	0.89	0.167	0.19
	5.11	0.68	0.127	0.24
	3.48	0.46	0.087	0.28
	1.77	0.24	0.044	0.36
	0.177	0.024	0.0044	0.68
10 Gelatine	20	2.66	....	0.51
	13.3	1.77	....	0.53
	10.0	1.33	....	0.56
	6.7	0.89	....	0.60
	1.82	0.242	....	0.65
	0.39	0.052	....	0.75
	0.010	0.0132	....	0.79
11 Ivory Soap	5	0.67	....	0.10
	3.5	0.47	....	0.18
	2.3	0.31	....	0.29
	0.4	0.053	....	0.68
12 Castile Soap	4.2	0.56	....	0.098
	2.7	0.35	....	0.20
	0.5	0.067	....	0.56

sodium phosphate, sodium carbonate and sodium silicate are also effective substances, and are much superior to the remaining substances in this group. These four substances and soaps are known to be especially valuable as cleansing agents. The effect of soap is not shown in Fig. 5, but is shown in Fig. 6. It is interesting to note that at very low concentrations, *viz.*, less than 5 g. per L., castile and ivory soaps are far more effective than all other sub-

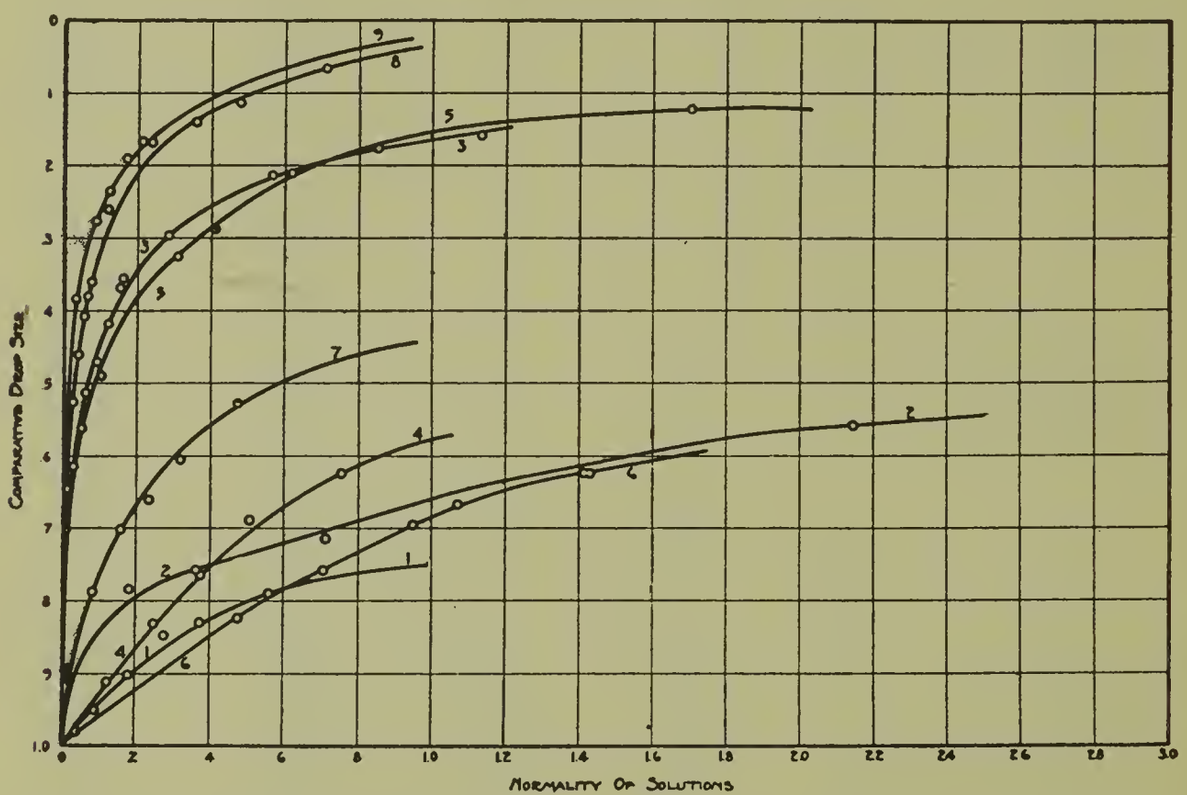

FIG. 4. Comparative drop size of solutions of substances used in alkaline metal cleaners.

The size of drops formed by the solution on issuing below Mobiloil E at 83° C., divided by the size of drops formed by distilled water under the same condition, are plotted as ordinates. The concentrations of the solutions used expressed as normality are plotted as abscissas. The substances used are indicated by numbering the curves.

Curve 1 $Na_2SO_4 . 10H_2O$	Curve 4 $Na_2HPO_4 . 12H_2O$	Curve 7 $Na_2B_4O_7 . 10H_2O$
Curve 2 $NaHCO_3$	Curve 5 Na_2CO_3	Curve 8 $Na_3PO_4 . 12H_2O$
Curve 3 Sodium Silicate	Curve 6 $NaHSO_4$	Curve 9 NaOH

stances tested except sodium hydroxide. Presumably the same comparison would hold for the more soluble soaps. Gelatine, an organic colloidal substance, is much less effective than soaps.

Table II presents data obtained in testing solutions of various mixtures, in each case keeping the total concentration (by weight) of dissolved substances constant. One set of experiments was at room temperature, the other set at 83° C. These data are presented graphically in Fig. 7. Comparative drop sizes are plotted

TABLE II.

Relative drop size of solutions of two substances.

I. Concentration 17.4 g./L. or 2.32 oz./gal.

Materials	Borax	Trisodium Phosphate	Comparative Drop Size at 26° C.
Concentrations g. per L.	17.4	0	0.64
	14.5	2.90	0.63
	13.1	4.35	0.62
	10.2	7.25	0.54
	7.25	10.2	0.50
	2.90	14.5	0.20
	1.45	16.0	0.15
	0	17.4	0.059

II. Concentration 8.18 g./L. or 1.09 oz./gal.

Materials	Soda Ash	Trisodium Phosphate	Comparative Drop Size at 83° C.
Concentrations g. per L.	0	8.18	0.36
	1.64	6.54	0.36
	3.27	4.91 (86°)	0.34
	4.91	3.27	0.34
	6.54	1.64	0.37
	8.18	0	0.34

III. Concentration 8.18 g./L. or 1.09 oz./gal.

Materials	Sodium Hydroxide	Trisodium Phosphate	Comparative Drop Size at 83° C.
Concentrations g. per L.	0	8.18	0.36
	1.64	6.54	0.26
	3.27	4.91	0.21
	4.91	3.27	0.17
	6.54	1.64	0.15
	8.18	0	0.17

IV. Concentration 8.18 g./L. or 1.09 oz./gal.

Materials	Soda Ash	Sodium Hydroxide	Comparative Drop Size at 83° C.
Concentrations g. per L.	8.18	0	0.39
	6.54	1.64	0.23
	4.91	3.27	0.20
	3.27	4.91	0.17
	1.64	6.54	0.16
	0	8.18	0.17

as ordinates, and relative percentages of substances in the solution as abscissas. With the mixtures $Na_3PO_4.12H_2O$ and NaOH, $Na_3PO_4.12H_2O$ and Na_2CO_3, NaOH and Na_2CO_3, almost a straight line relation exists. While a slight minimum point is indicated, this is perhaps due to a rise in temperature noted in two cases and to experimental error, which is proportionally large in these experiments, since the difference in the surface tension

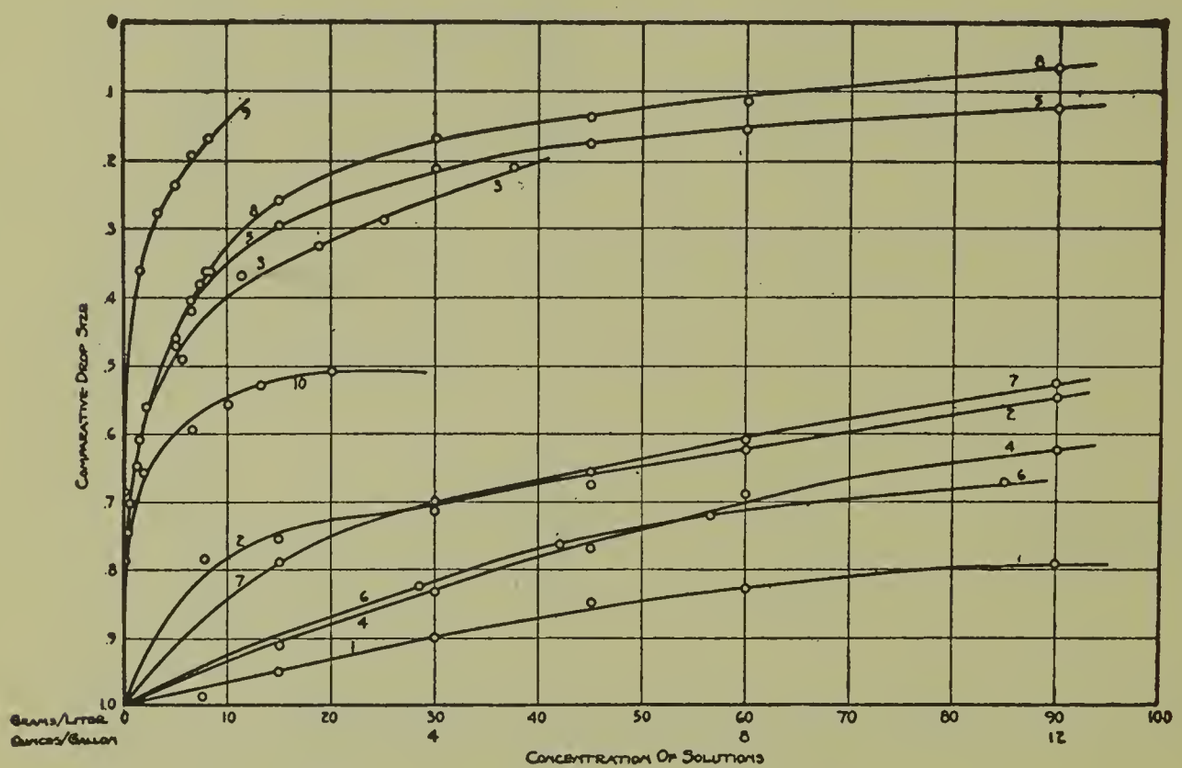

FIG. 5. Comparative drop size of solutions of substances used in alkaline metal cleaners.

The size of drops formed by the solution on issuing below Mobiloil E at 83° C., divided by the size of drops formed by distilled water under the same condition, are plotted as ordinates. The concentrations of the solutions used, expressed as grams of dissolved substance per liter of solution, and as ounces of dissolved substances per gallon of solution, are plotted as abscissas. The substances used are indicated by numbering the curves.

Curve 1 $Na_2SO_4.10H_2O$
Curve 2 $NaHCO_3$
Curve 3 Sodium Silicate
Curve 4 $Na_2HPO_4.12H_2O$
Curve 5 Na_2CO_3
Curve 6 $NaHSO_4$
Curve 7 $Na_2B_4O_7.10H_2O$
Curve 8 $Na_3PO_4.12H_2O$
Curve 9 NaOH
Curve 10 Gelatin

lowering of the two pure substances is slight. The mixture of $Na_3PO_4.12H_2O$ and $Na_2B_4O_7.10H_2O$ is interesting. In this case the difference between the surface tension lowering of the two substances is large. Adding a slight proportion of borax to a pure trisodium phosphate solution greatly lowers the effectiveness of the solution, but on the other hand adding trisodium phosphate to a solution of borax does not materially increase the effectiveness of the solution for cleaning.

TABLE III.

Relative drop size of solutions of a single substance at various temperatures.

A. Trisodium Phosphate—8.18 g./L.

Temp. °C.	Comparative Drop Size		
	Standard: H_2O at 26° C.	Standard: H_2O at 83° C.	Standard: H_2O at Same Temperature
26	0.60	0.87	0.60
40	0.45	0.65	0.49
63	0.30	0.44	0.38
83	0.25	0.36	0.36
91	0.24	0.35	0.36

B. Soda Ash—8.18 g./L. or 1.09 oz. per gal.

Temp. °C.	Comparative Drop Size		
	Standard: H_2O at 26° C.	Standard: H_2O at 83° C.	Standard: H_2O at Same Temperature
26	0.60	0.86	0.60
40	0.46	0.66	0.50
63	0.35	0.51	0.44
83	0.28	0.40	0.40
93	0.27	0.39	0.39

C. Disodium Phosphate—45 g. per L. or 6.00 oz. per gal.

Temp. °C.	Comparative Drop Size		
	Standard: H_2O at 26° C.	Standard: H_2O at 83° C.	Standard: H_2O at Same Temperature
28	0.73	0.97	0.73
39	0.66	0.88	0.73
53	0.61	0.80	0.76
74	0.56	0.73	0.68
87	0.52	0.68	0.68

D. Water.

Temp. °C.	Comparative Drop Size		
	Standard: H_2O at 26° C.	Standard: H_2O at 83° C.	Standard: H_2O at Same Temperature
26	1.00	1.44	1.00
40	0.91	1.32	1.00
63	0.80	1.16	1.00
83	0.69	1.00	1.00
93	0.68	0.93	1.00

Table III presents data obtained by the drop size of solutions of a single substance, at a single concentration, against Mobiloil E at different temperatures.

These data are presented in Fig. 8, comparative drop size being plotted as ordinates, and temperatures as abscissas. These curves show that the drop size decreases rapidly with increasing temperature until a temperature of about 80° C. is reached, after which the effect is less pronounced. It is interesting to note that boiling

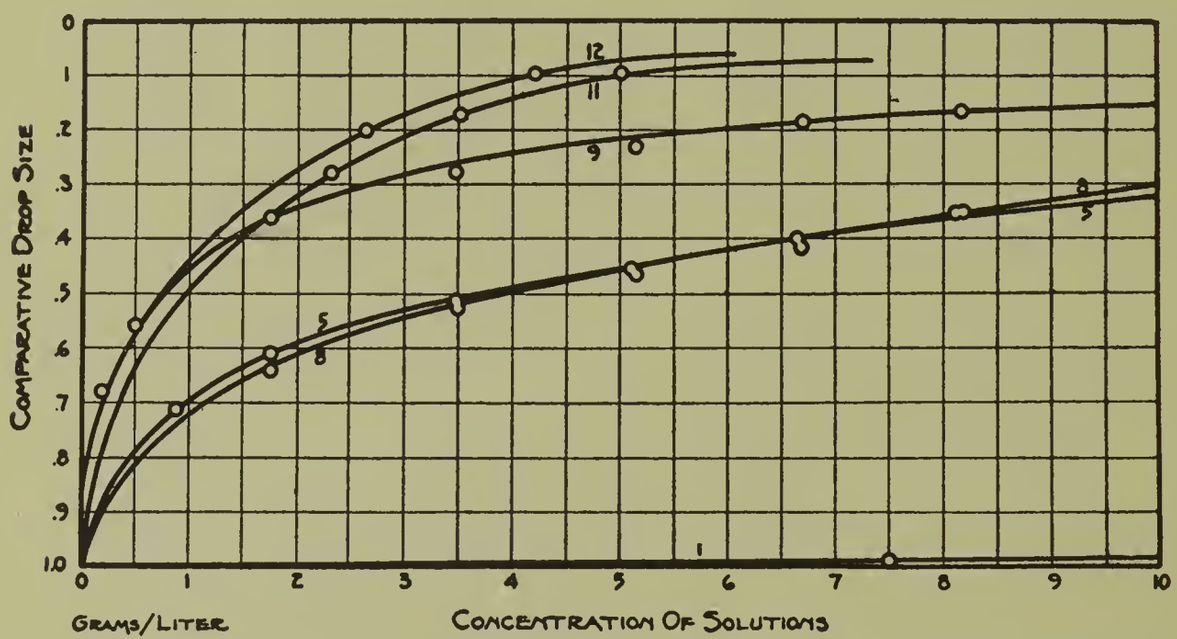

FIG. 6. Comparative drop size of solutions of substances used in alkaline metal cleaners.

The size of drops formed by the solution on issuing below Mobiloil E at 83° C., divided by the size of drops formed by distilled water under the same condition, are plotted as ordinates. The concentrations of the solutions used, expressed as grams of dissolved substance per liter of solution, and as ounces of dissolved substances per gallon of solution, are plotted as abscissas. This figure shows, on an expanded scale of abscissas, data on the lower concentrations of some solutions depicted in Fig. 5. The substances used are indicated by the numbering of the curves.

Curve 1 $Na_2SO_4 . 10H_2O$ Curve 8 $Na_3PO_4 . 12H_2O$ Curve 11 Ivory Soap
Curve 5 Na_2CO_3 Curve 9 NaOH Curve 12 Castile Soap

water is about as effective as a cold solution of 1 oz. per gal. of a so-called good cleaner.

Table IV gives data showing the viscosities of Mobiloil E at different temperatures, and also the viscosities of various mixtures of Mobiloil E and a petroleum spirit. The petroleum spirit is the grade sold as sunoco spirits, and had a progressive boiling point lying between 295° F. and 405° F. These results are presented in Fig. 9. Saybolt viscosities are plotted as ordinates against two sets of abscissas. The abscissas for curve (A) are compositions

TABLE IV.

Viscosity of Mobiloil E and solutions of Mobiloil E and petroleum spirits.

Material in Receiver	Oil		Oil-Spirit Solution			
	Temp. °C.	Viscosity (Saybolt)	Viscosity (Saybolt)	Per Cent Oil	Per Cent Petroleum Spirit (Sunoco)	Temp. °C
Gargoyle Mobiloil E at.	39	216	99	80	20	26
" " " "	54	120	65	70	30	26
" " " "	60	85	51	60	40	26
" " " "	69	64	38.5	40	60	26
" " " "	81	57	32	20	80	26
" " " "	92	52	28	.....	100	26

TABLE V.

Comparison of relative drop size and viscosity of oil.

Material	Saybolt Viscosity	Oil-spirit Mixtures 26° C.		Drop Size	Equivalent Temperature of Oil °C.	Drop Size
		Per Cent Oil	Per Cent Spirit			
Trisodium Phosphate, 8.2 g. per L.	125	85	15	0.55	53	0.52
	99	80	20	0.47	57	0.48
	65	70	30	0.46	68	0.41
	60	63	37	0.37	75	0.38
Soda Ash, 8.2 g. per L.	125	85	15	0.56	53	0.55
	99	80	20	0.54	57	0.52
	65	70	30	0.48	68	0.46
	60	63	37	0.40	75	0.43
Disodium Phosphate, 45 g. per L.	125	85	15	0.85	53	0.80
	99	80	20	0.80	57	0.79
	65	70	30	0.76	68	0.75
	60	63	37	0.71	75	0.72

of mixtures of petroleum spirit and Mobiloil E at 26° C., and for curve (B) are temperatures of Mobiloil E. Thus if values of abscissas corresponding to the same ordinates are read from curves A and B, the value from curve A gives the composition of oil-spirit mixture, which has the same viscosity at 26° C. as Mobiloil E alone has at the temperature read from curve B.

Table V presents the data on the surface tension measurements of $Na_3PO_4 . 12H_2O$, Na_2CO_3 and $Na_2HPO_4 . 12H_2O$ solutions with oil and with oil-spirit mixtures. Column 1 gives the material used. Column 2 gives the viscosity of the oil or oil-spirit mixture in the receiver. Column 3 gives the composition of the oil-spirit mixture which at 26° C. has the viscosity shown in column 2.

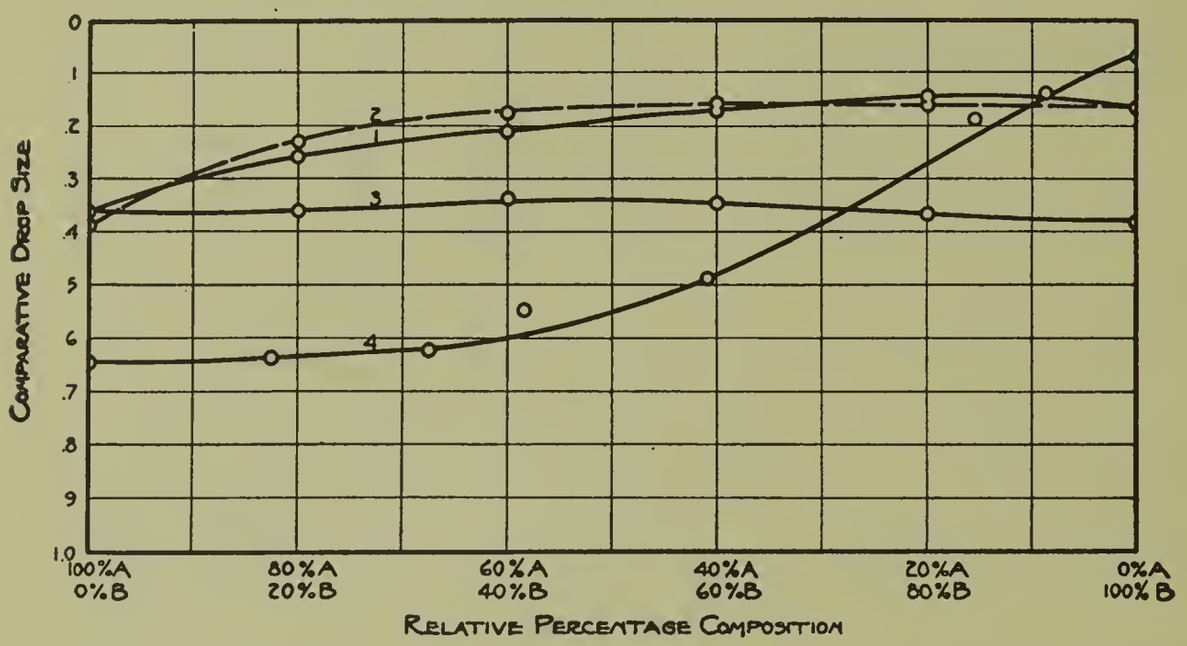

FIG. 7. Comparative drop size of solutions of mixtures of some substances commonly used in alkaline metal cleaners.

Comparative drop sizes of the solution on issuing below Mobiloil E are plotted as ordinates. The relative percentages of the substances used in the solutions are plotted as abscissas.

Curve No.	Substances Used		Total Conc. g. per L.	Temp. of Experiment °C.
	A	B		
1	$Na_3PO_4 . 12H_2O$	NaOH	8.2	83
2	Na_2CO_3	NaOH	8.2	83
3	$Na_3PO_4 . 12H_2O$	Na_2CO_3	8.2	83
4	$Na_2B_4O_7 . 10H_2O$	$Na_3PO_4 . 12H_2O$	17.4	26

Column 4 presents the comparative drop sizes of solutions at 26° C. in these oil-spirit mixtures calculated against the drop size of water in Mobiloil E at 83° C. Column 5 gives that temperature of Mobiloil E at which the oil would have the viscosity indicated in column 2. These results were read from the curves of Fig. 9 (see Table IV). In column 6 are presented the comparative drop sizes of solutions in Mobiloil E at temperatures given in column 5. These results are shown graphically in Fig. 10. Comparative drop

sizes are plotted as ordinates and Saybolt viscosities as abscissas. Smooth curves were drawn using the two values at each viscosity as a guide. It is indicated that surface tension lowering is directly a function of the viscosity of the oil used, and is a major function of the temperature only insofar as the viscosity changes with the temperature.

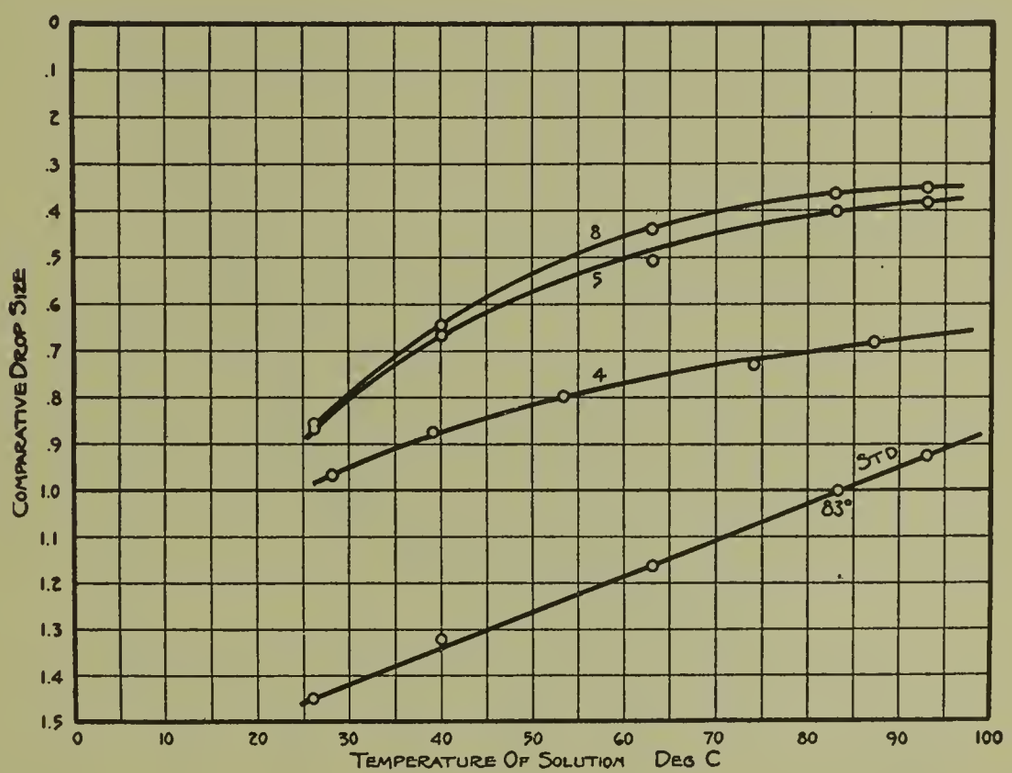

FIG. 8. Effect of temperature of experiment on comparative drop size.

The comparative drop sizes, calculated by dividing the drop sizes of the solutions, at the temperatures shown, by the drop size of water issuing below Mobiloil E at 83° C., are plotted as ordinates. The temperatures of the experiments are plotted as abscissas. The standard graph shown is that of water.

Curve No.	Substance	Conc. of Solution g. per L.
4	$Na_2HPO_4 . 12H_2O$	45.0
5	Na_2CO_3	8.2
8	$Na_3PO_4 . 12H_2O$	8.2

In enumerating the qualities of a metal cleansing composition, it must be remembered that surface tension lowering is not the only important consideration. For instance it is generally known that soap is the most effective emulsifying agent used for cleansing metal. However, even if soap were enough cheaper to compete with the alkaline salts, it would hardly be advisable to do cleansing with this substance alone. Trisodium phosphate solutions after

being used for removing oil from metal will, upon standing for a few hours, give up the oil, due to breaking down of the emulsion. A soap solution on the other hand, tends to form too stable an emulsion, and hence grows rapidly weaker in soap and in cleansing power with use. The emulsion formed by a good cleaning solution should be unstable, so that after a few hours of disuse the oil will

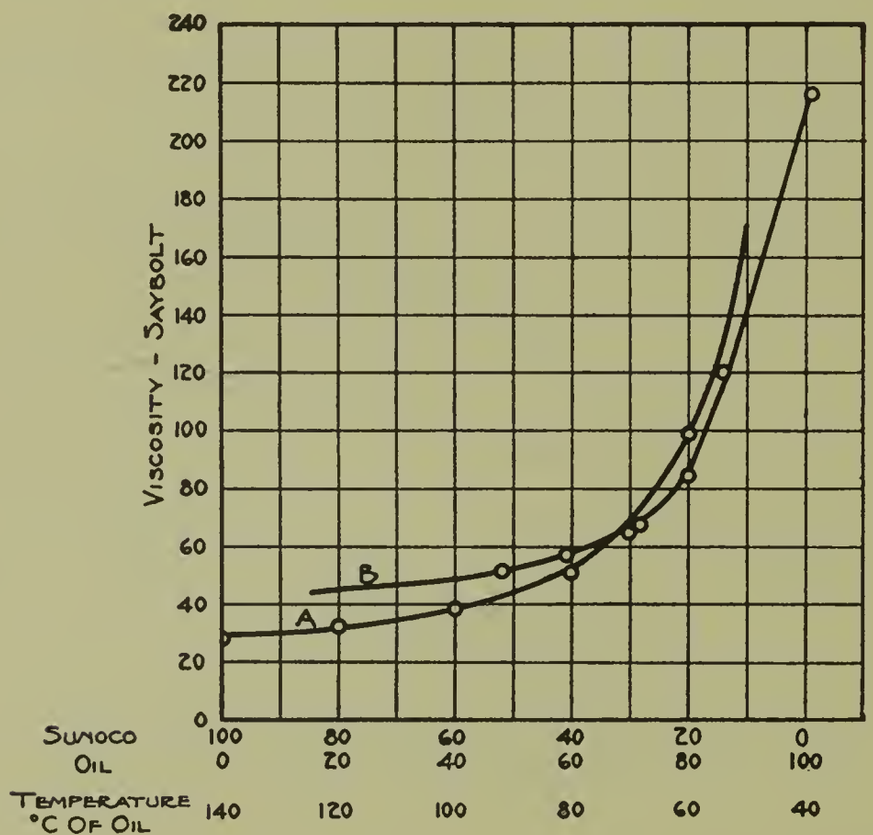

FIG. 9. Viscosity of oils used in determining comparative drop sizes.

Curve B shows as abscissas the temperatures at which the Mobiloil E used has the Saybolt viscosities plotted as ordinates. Curve A shows the compositions of mixtures of sunoco spirit and Mobiloil E which have the viscosities at 26° C. that are plotted as ordinates for this curve. From these curves it is possible to determine the composition of an oil-sunoco spirit mixture which will have the same viscosity at 26° C. as Mobiloil E has at any temperature from 50 to 120° C.

separate and rise to the surface of the tank. The solution may be skimmed before starting work in the morning, thus rendering the solution effective for continued work. If the solution is so skimmed, most of the weakening of the cleaner up to a point where the amount of accumulated greasy dirt becomes too great, is due to solution being spilled or carried out on the work.

Sodium hydroxide exhibits the tendency of forming stable emulsions to a less degree than solutions of soaps, but to a greater degree than solutions of trisodium phosphate or sodium carbonate. A series of six solutions of mixtures of trisodium phosphate

and sodium hydroxide were made up. The total concentration of these solutions was maintained constant and the composition was varied from pure $Na_3PO_4 . 12H_2O$ to pure NaOH. These solutions were placed in test tubes and shaken with oil. After standing for two weeks at room temperature the aqueous portions had a milky appearance. The degrees of milkiness varied from almost a

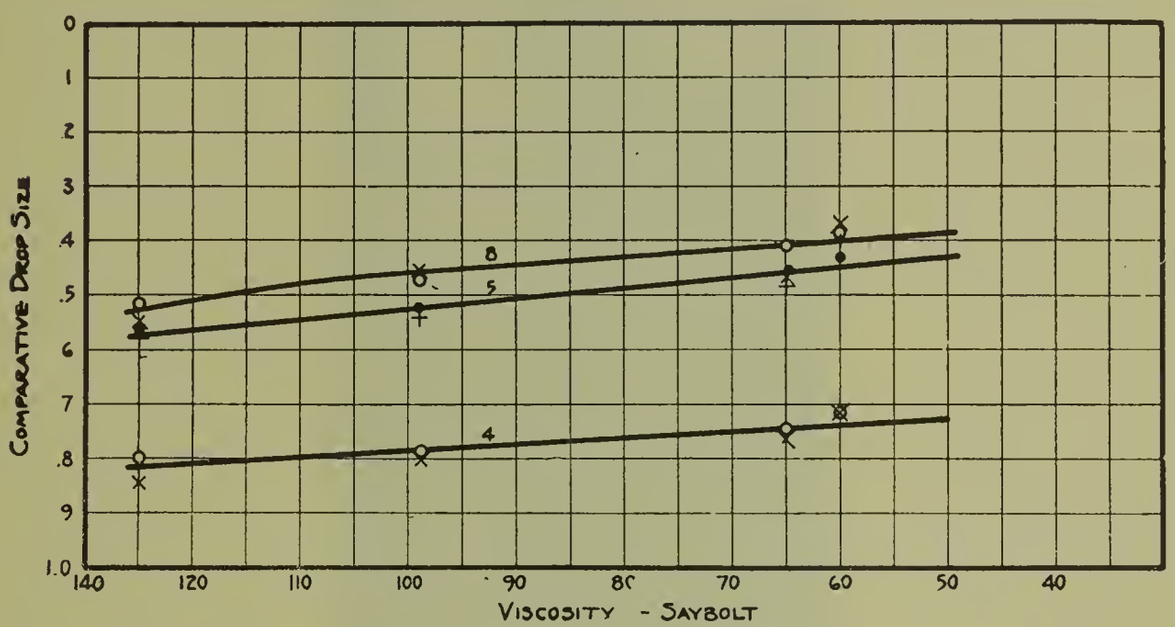

FIG. 10. Comparative drop sizes of solutions issuing below oil of various viscosities.

The comparative drop sizes are plotted as ordinates. Saybolt viscosities are plotted as abscissas. The oils used were Mobiloil E at various temperatures, and mixtures of Mobiloil E and sunoco spirit at 26° C. The data are taken from Table V. The points plotted as circles refer to measurements made with Mobiloil E at various temperatures, while the crosses refer to oil-spirit mixtures. The curves show that the viscosity of the oil determines the comparative drop size obtained with any given cleaning solution.

Curve No.	Substance	Conc. of Solution g. per L.
4	$Na_2HPO_4 . 12H_2O$	45.0
5	Na_2CO_3	8.2
8	$Na_3PO_4 . 12H_2O$	8.2

clear solution, in the case of trisodium phosphate, to a decidedly milky solution, in the case of sodium hydroxide. After standing a further period of 8 months the same progressive differences in turbidity persisted. The appearance of the two extreme tubes is shown in the unretouched photograph, Fig. 11. Tube A contains oil and the solution of trisodium phosphate, and tube B oil and the solution of sodium hydroxide.

Another function of the alkaline cleaner is that of water soften-

ing. For this purpose phosphates, carbonates, borates and in fact almost any of the alkaline salts will function satisfactorily. Perhaps this is the reason that borax is used in so many of the light

FIG. 11. Permanence of emulsions of Mobiloil E with solutions of trisodium phosphate and of sodium hydroxide.

The photographs show the appearance of two such emulsions after standing eight months. Tube A contains oil and a solution of trisodium phosphate and has become nearly clear on standing, while tube B, which is much more cloudy, retains much of the original emulsion of sodium hydroxide and oil.

duty cleaners, although surface tension measurements indicate that it has little value as a cleaner. There is no reason why it should be present, since it renders trisodium phosphate less effective, and since trisodium phosphate is equally valuable as a water softener.

Still another factor to be considered is that of rinsibility of the cleaning solution. Semi-quantitative tests in rinsing showed NaOH and Na_2CO_3 in solution to be almost three times as persistent as a solution of $Na_3PO_4 . 12H_2O$ of equal concentration by weight. This is probably due in part to the fact that in solutions of equal concentrations the solution of trisodium phosphate contains only about 43 per cent as much anhydrous solid substance. Further, the difficulty of rinsing free from sodium compounds probably depends on the degree to which Na ions are adsorbed on the surface of the work. In solutions of sodium salts, equivalent in sodium content, the concentration of Na ions, would be greatest for solutions of NaOH, less for solutions of Na_2CO_3 and least for solutions of trisodium phosphate. The difficulty of rinsing varies in this same order.

Referring again to a consideration of soap, the addition of several per cent of soap may be depended upon to speed up the cleansing operation, and to remove grit which is not effectively removed by simple alkaline solutions. The soap must be frequently replenished. The types of soap usually used are oleic, stearic, resinic and linoleic. Their effectiveness seems to be a function of their solubility. Linseed oil soap is the most soluble and the most effective. Stearic acid soaps are the least soluble and are quite unsatisfactory.

In the average plant of such a size that large amounts of cleaners are used annually, it may be advisable either to buy cleaners on specification, or to mix the cleaners in the plant. It is often possible to omit preliminary mixing of the cleaning composition, by merely dissolving technical materials in the desired proportions. In cases where this can be done, a saving of 50 per cent of the cleaner costs is readily accomplished.

As a guide in mixing cleaners in the plant, the following considerations may be of assistance.

1. NaOH and $Na_3PO_4 . 12H_2O$ are the most effective heavy chemicals easily obtainable. NaOH is strongly alkaline, whereas $Na_3PO_4 . 12H_2O$ is only mildly alkaline. The latter substance is less apt to stain work being cleaned, and is far more easily rinsed from the work.

2. A mixture of NaOH and Na_2HPO_4, mol for mol, may be

used in place of Na_3PO_4 with equally good results, if the cleaner is not to be used in small amounts for such purposes as hand scrubbing. In this case there is danger of attack of the hands by the caustic soda if the cleaner is not mixed uniformly.

3. Soaps are very effective cleaners, particularly for the removal of grit. Soaps are hard to rinse from the work and are usually comparatively expensive. The soaps of less saturated fatty acids form the better cleaners.

4. Glycerine is very detrimental in a cleaner. Its presence is not evidenced by water-break on the work, but it cannot be completely removed by rinsing. Plated work cleaned with a solution containing even small amounts of glycerine will peel easily. Hence fats should not be added to a strongly alkaline cleaner to produce desired soaps.

5. Water glass or sodium silicate may be used as an effective mildly alkaline component of a cleaner, and as a substitute for soap.

6. The cleaner should be kept at as high a temperature as possible, if rapid thorough cleansing is to be obtained.

7. Agitation of the solution is desirable, and aids greatly in cleansing. Air agitation does, however, tend to cool the solution, and may be troublesome from the standpoint of causing the solution to foam over the top of the tank.

8. The use of direct electric current is an aid to cleansing, but is not very effective if the current density is less than 10 amp. per sq. ft. (1.08 amp./sq. dm.) of surface to be cleaned. Higher current densities are desirable. Generally it is preferable to make the work the cathode, though there are exceptions to this rule, *viz.*, cleansing nickeled work preparatory to replating with nickel.

9. If the oil is skimmed from the surface of the tank each morning, and the heavy dirt removed or allowed to settle under a false bottom, the life of the cleaner will be lengthened, and it will give better service.

It will be apparent that these same factors will enter into consideration if some commercial composition is to be selected as a cleaner from a group of such compositions of known chemical composition.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, President Hinckley in the Chair.

IMPROVEMENTS IN ELECTROLYTIC REFINING DURING THE LAST DECADE.

By S. Skowronski.[1]

Upon reviewing the improvements made in electrolytic refining during the last decade, we are today obliged to divide the subject into two parts; the first part dealing with the refining of a crude metal anode into a refined cathode, which process is strictly "electrolytic refining," and the second part taking up the recovery of metals from solutions obtained from the ores, concentrates or metallurgical products, using various solvents. Processes of the second part involve insoluble anodes with correspondingly high voltages. For want of a better term, these processes are known as "electro winning" or "electrolytic recovery."

I. ELECTROLYTIC REFINING OF METALS.

Copper. The industry of electrolytic refining of copper is now in its fifth decade, consequently the theory as well as the practical application of same has been well developed.

Owing to the intensive period of production represented in the years from 1914 to 1918 inclusive, there has been a great increase in the refinery capacity of this country. While in 1914 the refinery capacity of the United States was 1,778 million pounds of copper, it is today (1924) 2,800 million pounds, an increase of 57 per cent or over 1,000 million pounds of copper.

The tendency has been toward centralization, and individual refineries have grown to such an extent that they now handle enormous productions. One refinery alone has a capacity greater than the yearly production of copper in the United States prior to 1900, and greater than the yearly world's production of copper prior to 1893.

With the increased size of the refineries the current passed

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through the tanks has increased until today currents of 10,000 amp. per circuit are not unusual. The current density, however, remains about the same, the average being from 18 to 20 amperes per sq. ft. (2 to 2.2 amp. per sq. dm.) of cathode area. Some of the refineries generating their own power, have found it more economical to run as low as 15 amp. per sq. ft. (1.7 amp. per sq. dm.).

Power being the main item of cost, particular attention has been paid to the economic generation of same. Hydro-electric power is now used for about one-third of the refinery capacity, and experimentation is now being carried on to do away with reciprocating engines and direct current generators, the aim being to generate alternating current by means of turbines and to convert it to direct current at the tank houses by rotary converters or motor generator sets.

All the new additions to the refinery capacity are using the multiple system, consequently the percentage of copper refined by the series system is becoming less. It is realized, however, that for certain brands of blister copper containing only small amount of impurities the series system has economic advantages over the multiple system, and the largest refinery, in the United States, is now using both systems.

The recovery of the various by-product metals present in the blister copper is now an important function of the refineries, not only for the value of the metals themselves but also for the absolute necessity of preventing an accumulation of these impurities in the refining cycle.

A wet method of slime treatment for the recovery of silver and gold has been tried on a commercial scale, but failed. Whatever merit this process might have had in the elimination of stack losses of precious metals has been counteracted by the universal adoption of the Cottrell precipitator on the cupel or doré furnaces.

Zinc. The electrolytic refining of crude spelter into refined zinc, using a zinc sulfate electrolyte, was attempted on a commercial scale, and while the process was scientifically successful, high-grade metal being produced, it was a commercial failure due to the fact that no valuable by-product metals could be recovered, and the difference in price between low-grade and high-grade zinc was not sufficient to cover the cost of refining.

In this connection it must be emphasized that electrolytic refining processes are necessarily expensive processes, the capital invested per unit of capacity being far greater than that required by the ordinary fire process. In order to be commercially successful, and to compete with fire processes, electrolytic refining must do one or both of two things—it must find a ready market for the superior product it produces at a premium over that produced by the ordinary fire methods, or it must recover by-products to pay for at least part of the increased cost of production of the pure metal.

Lead. The Betts process for the electrolytic refining of lead has not made much headway in competing against the Parkes process, except in the case of lead bullion carrying bismuth. The Parkes process does not remove bismuth. Electrolysis by the Betts process is also superior to the Pattinson process.

The three plants now using the Betts process are The Consolidated Mining and Smelting Co., at Trail, British Columbia, The United States Lead Refinery Co., at East Chicago, Ind., and the Omaha plant of the American Smelting and Refining Co., with respective daily capacities of 120, 100 and 30 tons. The Omaha plant of the American Smelting and Refining Co. is using the Parkes process for refining lead bullion low in bismuth, and the electrolytic process for high bismuth bullion.

Lead has an advantage over the base metals in that owing to its high atomic weight it has a high electrochemical equivalent. The refineries are obtaining from 16 to 22 lb. (7.3 to 10 kg.) of lead per kw.-hr. The electrolytic process is handicapped with an expensive electrolyte, hydrofluosilicic acid, and while the electrolyte never needs to be purified, since all the impurities in the lead anodes are electronegative to lead, the mechanical losses of the electrolyte are as high as from 4 to 10 lb. per ton (2 to 5 kg. per metric ton) of bullion refined.

Considerable experimentation has therefore been done on the problem of a cheaper electrolyte, and the organic acids and compounds, such as the sulfonates, seem to offer the best possibilities for commercial work.

Tin. The electrolytic refining of tin on a large scale became commercial during the last decade, and is a credit to the Ameri-

can metallurgists, who made it possible under a period of stress. Starting with an expensive electrolyte, fluosilicic acid, there has been a gradual substitution of sulfuric acid and sodium sulfate, with a corresponding lowering of costs. In common with all electrolytic processes, the cathode deposit of refined tin is of the highest purity, yet it can not command a premium over the Straits or Banca tin.

In the smelting of tin ores, the impurities are not removed, and the electrolytic process is particularly suitable for the treatment of Bolivian concentrates, which carry impurities which can not be removed by any other process. Economic conditions in the tin industry at the present moment are such that the plant which developed the electrolytic process is now shut down, and there is no tin industry in this country today, the market being completely dominated by English interests.

Nickel. The commercial development of the Hybinette process for the refining of nickel marks the progress in nickel metallurgy during the last decade. This process is in use in Norway and Ontario, Canada. The Hybinette process depends upon the roasting of a high-grade copper-nickel matte, leaching most of the copper out with sulfuric acid, and the reduction of the residue to a nickel anode carrying only a small quantity of copper. The anode is electrolyzed in a double compartment cell, the anolyte containing whatever copper was present in the anode, being passed over sponge nickel or matte to cement out the copper and the resulting copper-free liquor being used as the catholyte.

The International Nickel Co. dismantled their plant at Bayonne, N. J., and built a new refinery at Port Colborne, Canada. This company has greatly extended its electrolytic process for the refinery of nickel, the economic factor being the precious metals recovered from the nickel anodes. Nickel bullion not only carries a small amount of gold and silver, but also a percentage of the platinum group of metals higher than that of copper bullions. It is the recovery of palladium, platinum, iridium and rhodium, at their present high prices, which makes the refining of nickel of economic interest.

The electrolytic refining of nickel, however, does not bring about any separation from cobalt, and the resulting product has

to compete with the high-grade product obtained by the carbonyl distillation process, known as the Mond process, which method of refining also recovers the precious metal values. An important factor in comparing the two processes is the profitable disposal of the great tonnage of copper sulfate obtained by the Mond process.

Ductile electrolytic nickel has been made by the Madsen process. This process, depending upon the keeping of hydrogen and organic compounds out of the cathode deposit, makes a cathode metal of high malleability and ductility, which is a commercial advantage in a metal like nickel.

Precious Metals. While electrolytic parting of doré metal has been greatly extended, owing to the construction of a large custom refinery at Pachuca, Mexico, using the Thum system, a few of the refineries are still using the old method of sulfuric acid parting, claiming that their costs are lower than the electrolytic. Local conditions, and the disposal and the market for copper sulfate are the determining factors. No radical changes have been made in either the Thum or Moebius system of electrolytic parting. The use of copper nitrate in the electrolyte up to 30 g. per L. of copper has been found necessary, to improve the conductivity of the electrolyte, and the silver contents are kept at not less than 40, and generally at not less than 60 g., per L. Owing to the liability of contaminating the cathode deposit with tellurium, free nitric acid is now seldom used in the electrolyte.

The increased price of platinum and palladium have finally forced on the refineries the adoption of the Wohlwill electrolytic gold process. This process, in use for a long time at the government refineries, consists in electrolyzing a gold anode in an electrolyte of 10 per cent hydrochloric acid and 10 per cent gold, as gold chloride, at 75° C. The cathode gold is exceedingly pure, averaging 999.75 fineness. The platinum and palladium are allowed to build up in the electrolyte to 50 g. per L. An interesting development is the use of a superimposed alternating current, on the direct current used for refining. This allows the use of anodes of a higher silver content than would be possible using direct current alone, and with less generation of chlorine gas. This modification of the Wohlwill process is used by all the gov-

ernment refineries, but has not as yet been adopted by the custom refineries, as they are able to remove the silver by fuming with sulfuric acid.

Bismuth. One of the lead refineries is producing electrolytic bismuth from the electrolysis of a bismuth chloride and hydrochloric acid electrolyte. The cell used is similar to the Thum cell used for the parting of doré metal in the silver refineries. At the time of the high price of antimony metal, several electrolytic processes for the recovery as well as the refining were experimented with, but none of them proved commercial.

Iron. The Western Electric Co. at their Hawthorne, Ill., plant are making 25,000 lb. (11,340 kg.) weekly of electrolytic iron for use in the manufacture of magnet cores. The tank house for iron refining closely resembles that of a copper refinery. The electrolyte consists of ferrous sulfate and ammonium chloride, the current density is 16 amp. per sq. ft. (1.8 amp. per sq. dm.). The anode is mild steel, and the cathode a polished steel sheet. After the deposit has reached a thickness of 0.125 to 0.25 in. (3 to 6 mm.) it is stripped off. Due to the hydrogen content, the cathode metal is brittle. It is cut up and ground in a ball mill, after which the hydrogen is removed by annealing.

The economic factor in this particular instance, is the very high grade of iron produced, 99.97 per cent, which is necessary for the particular electromagnetic purpose for which it is used. Such iron can not be made as cheaply by any other method.

At Grenoble, France, the Boucher process goes still further, and boiler tubes of iron are made by electrodeposition on a revolving mandrel. When it is considered how often this particular scheme has been tried in the case of copper, and failed, we are inclined to be somewhat sceptical as to the commercial future of the Boucher process. The facts are that the Boucher process has been in commercial operation in France for over ten years. The electrolyte is a ferrous chloride solution, the anodes are of cast iron, and the power consumption is from 0.25 to 0.33 h.p. year per ton (0.2 to 0.27 kw. year per metric ton) of tubes produced, which is equivalent to 0.8 to 1.0 lb. of iron per kw.-hr. (0.36 to 0.46 kg. per kw.-hr.).

The tubes after drawing from the mandrel are annealed to

remove the hydrogen. They are soft and ductile, and are much thinner than the usual tubes, which is claimed to be a decided advantage. In this connection it must be pointed out that whereas in ordinary drawing processes the thinner the tube, the more labor and work and therefore the greater the expense; in electrodeposition the thinner the material the lower the cost. There must, therefore, be a certain gauge or tube thickness at which the two processes, mechanical *vs.* electrolytic, balance each other in cost.

Germany is said to have substituted electrolytic iron for copper in the manufacture of shell bands, when forced to do so, owing to being unable to obtain copper.

II. ELECTROLYTIC RECOVERY OF METALS.

The outstanding achievement in the commercial electrolytic recovery of metals during the last decade has been the successful commercial recovery of copper and of zinc from the electrolysis of solutions obtained by the leaching of ores, concentrates and certain metallurgical products.

Recovery of metals from solutions, by electrolysis using insoluble anodes and dispensing with fire smelting, has been the aim of electrometallurgists for many years. The theories underlying the various processes, now in use, were well understood, but it needed the impetus of an extraordinary demand for metals at high prices, to utilize the theories, and to make the processes commercially successful.

Zinc. The electrolytic recovery of zinc from solutions has solved the problem of the treatment of certain complex zinc-lead-silver ores. Owing to the increase in the consumption of lead, and the depletion of known lead deposits, lead has this year (1924) been quoted as high as 10 cents a pound. The hydrometallurgy of zinc, with the subsequent recovery of high-grade zinc by electrolysis from sulfate solution, makes it possible to recover zinc, lead and silver from complex ores, at a far greater efficiency than has hitherto been considered possible by fire methods.

In the electrolytic recovery of copper and zinc, the cycle of electrodeposition, although undoubtedly the most important, is at the same time really the simplest. The various other opera-

tions of hydrometallurgy, such as concentration, roasting, leaching, and above all purification of solutions or electrolytes, are just as essential to the economic operation of the process as the electrolysis itself. What really made the hydrometallurgy of zinc possible was flotation, which concentrated values in the ore to a point where the roasting, leaching and electrolysis were economically possible.

Zinc differs from copper in that there is really no other commercial method or precipitant known to produce zinc metal from a solution other than that of electrolysis. We therefore find electrolytic zinc recovered on large commercial scale at the Great Falls plant of the Anaconda Copper Mining Co.; at the Trail smelter of the Consolidated Mining and Smelting Co., Canada; and at the Electrolytic Zinc Works of Risdon, Tasmania.

The process employed is essentially the same at all plants. The complex sulfide ores are concentrated by flotation, roasted and the resulting zinc oxide leached with sulfuric acid; either by a basic leach, which automatically removes iron from the solution, or by a slight acid leach, in which case the iron is subsequently oxidized and precipitated with lime. The resulting zinc sulfate solution is purified from all traces of the more electropositive metals by treatment with zinc dust. As zinc is electronegative to hydrogen, upon the removal of these metals depends the success of the electrolysis, and it is remarkable what small traces of impurities, if allowed to remain in the electrolyte, will ruin the efficiency of the electrolysis.

The tanks used for electrolysis are either of wood, lead lined, or of concrete, lined with asphalt. The anodes are of pure lead, and while it is possible to use starting sheets of zinc as cathode, it has been found more economical to use sheet aluminum blanks as cathode, and to strip the electrolytic zinc deposit at 48-hr. intervals. The current density used is about 20 amp. per sq. ft. (2.2 amp. per sq. dm.). The voltage is high, being 3.5 to 4.0 v. per cell, making the recovery of zinc per kw.-hr. unusually low, only from 0.5 to 0.7 lb. (0.23 to 0.32 kg.) of zinc. This makes the ratio of the power cost of electrolysis to the value of the metal far greater than the electrolysis of any other metal in aqueous solutions, and makes cheap power an absolute necessity for zinc electrolysis.

Considerable experimentation has been made on the use of high current density. (Tainton process.) The use of 100 or more amp. per sq. ft. (11 amp. per sq. dm.) allows a greater latitude in the composition of the electrolyte, both as to impurities and free acid content. This is accomplished at no increase in the power consumption, since the higher voltage, which would naturally be expected at the higher density, is counteracted by the increased conductivity of the electrolyte due to the higher acid content.

Cadmium. It is only a step from the electrolytic recovery of zinc to the electrolytic recovery of cadmium, and both the Electrolytic Zinc Works of Australia and the Anaconda Copper Mining Co. are recovering electrolytic cadmium as a by-product of the zinc refinery.

Copper. The principles underlying the electrolysis of pure copper sulfate solutions are of course well understood, and the hydrometallurgy of copper has been successfully developed during the last decade, due to economical leaching of oxidized ores in larger tonnages, with a minimum amount of sulfuric acid as solvent. So far, hydrometallurgy has not been economically successful in the treatment of sulfide ores. This is due to the fact that most of the sulfide ores carry a trace of silver, and to the high cost of roasting.

The two large plants recovering copper from solution by electrolysis are the Chile Copper Co., at Chuquicamata, Chile, and the New Cornelia Copper Co., at Ajo, Arizona. Active experiments in the hydrometallurgy of copper are at the present time being conducted at various plants, notably at that of the Union Miniére du Haut Katanga, in Africa.

Here again, as in zinc, the electrolysis of the solution is only one step of the cycle of operation, and in contradistinction to zinc there are other methods of recovering copper from solutions besides the electrolytic, notably cementation on some form of iron, or precipitation with sulfur dioxide gas under pressure. Electrolysis of the solution has the advantage of producing a high-grade product, needing only a melting down operation to obtain the commercial shapes.

The electrolytic process has the further advantage of regener-

ating the acid, about 1.5 lb. of sulfuric acid per pound of copper. The power consumption, however, is high, the average recovery with lead anodes being 0.75 – 1.25 lb. (0.34 – 0.57 kg.) of copper per kw.-hr., and is liable to be much higher if the impurities, particularly iron, are allowed to accumulate in the electrolyte, which is bound to occur in the ordinary cycle.

The hydrometallurgy of copper is quite complicated, and no one process is applicable to all ores; each individual ore is a problem by itself. In Chuquicamata, the surface ore is essentially a basic copper sulfate (brochantite), soluble in water, consequently the cost of acid is not a factor, and there would be a recovery of sulfuric acid if same could be used. The ore is unusually free from metallic impurities; therefore, the resulting copper is of an unusually high grade, comparable in every way with electrolytically refined blister copper. The ore, however, contains small amounts of chlorides and nitrates, and while most of the chlorine is removed before electrolysis, the problem is an electrolysis of copper sulfate and sulfuric acid containing nitrates and chlorides.

No lead can, therefore, be used in the construction of the plant, and the great problem has been the finding of suitable anode material to withstand the corrosive effect of the mixed acid. Magnetite anodes were first used, but did not prove successful. Duriron anodes gradually dissolved and built up iron in the electrolyte, and materially cut down production and increased costs by lowering the efficiency of the electrolysis. The problem has been efficiently solved by the introduction of the "Chilex" anode, developed by the company. This anode is essentially a copper silicide, compounded with small amounts of other metals, has a good conductivity and a remarkable resistance to the acid electrolyte of Chuquicamata, with the added advantage that what does go in solution does not contaminate and build up in the electrolyte.

At Ajo the problem has been the controlling of the impurities, chiefly iron, so that the efficiency of the electrolysis could be maintained at an economic figure. There are no nitrates in the ore, consequently lead anodes are used. On account of the iron present, sulfur dioxide gas as a depolarizer is used in the cycle of recovery. The current density is from 7 to 8 amp. per sq. ft. (0.8 to 0.9 amp. per sq. dm.); the voltage between electrodes 2.1; and 0.85 lb. (0.39 kg.) of copper is obtained per kw.-hr.

A great deal of experimentation is now under progress in this country on the hydrometallurgy of copper, with particular reference to the control of the soluble iron so as to obtain a greater output of copper per kw.-hr. Experimentally outputs of 4 to 5 lb. (1.8 to 2.3 kg.) of copper per kw.-hr. have been obtained, and the possibilities of more efficient electrolysis are recognized.

Some of the copper rolling mills have adopted electrolysis of their pickling solution, not only to recover the copper but to re-use the sulfuric acid as well. The aim is not to remove completely the copper, but rather to keep the electrolytic tanks in cycle with the pickling tanks, so as to keep the pickling liquors at a fairly constant composition, 1 to 3 per cent copper, 14 to 20 per cent sulfuric acid.

Lead. A great deal of experimental work with the electrolytic recovery of lead has been done on the hydrometallurgy of lead, with as yet no commercial results, but good possibilities owing to the present scarcity and high price of lead. The electrolytic recovery of lead from the leached tailings of the hydrometallurgy of zinc offers good possibility, particularly since the plants are already equipped for electrolytic work and have cheap power. The electrolyte experimented with has been mainly lead chloride, soluble in a strong brine (salt) solution. Both the anode and cathode are of iron. The efficiencies have been good and the power consumption remarkably low, 12 to 14 lb. (5.5 to 6.4 kg.) of lead being obtained per kw-hr.

When it is considered that in the electrolytic recovery of zinc 0.7 lb. (0.3 kg.) per kw.-hr. is considered good practice, and even in copper refining with a soluble anode (multiple system) 8 lb. of copper per kw.-hr. is considered good, the commercial possibilities of recovering lead by electrolysis can readily be appreciated. The difficulty has been that in the brine electrolyte the cathode deposit is of a spongy nature, readily detaches itself from the cathodes, contains impurities, and on melting down into metal as much as 40 per cent of dross is formed.

Iron. There has been considerable research work on the hydrometallurgy of iron, and the recovery of iron from the resulting leach liquors by electrolysis. While the processes used give promise of success, they have not as yet been adopted commercially.

Before closing a tribute should be paid to the progress made during the last decade in another branch of electrodeposition—the deposition of metals from fused electrolytes, which is limited to the deposition of the strongly electropositive metals. For some reason this has always been considered as electric furnace work, rather than electrodeposition, but the laws underlying the practical operation are the same whether the bath is an aqueous bath or a fused or molten bath. It is hoped that the electrodeposition section will consider this ever-growing and important field of metallurgy to be within their jurisdiction, and in some meeting in the near future hold a symposium on the electrodeposition of metals from fused electrolytes.

Electrodeposition of metals from aqueous solutions has to compete with fire methods of reduction, but in the electrodeposition from fused electrolytes there is no competition; the entire commercial field is electrolytic reduction.

Aluminum. The entire output of aluminum is obtained from the electrolysis of a solution of refined bauxite, Al_2O_3, in a fused bath of cryolite, Na_3AlF_6.

Calcium, which has found some use as a lead hardener, is obtained from the electrolysis of the fused chloride.

Metallic sodium is obtained by the electrolysis of molten caustic soda.

Magnesium. In 1914 there was no magnesium industry in this country. With the stopping of imports the metal was quickly obtained by electrolysis of the fused chloride. A recent development in magnesium is the electrolysis of magnesium oxide in a bath of magnesium fluoride. This process now is used commercially and promises to solve the technical application of magnesium as a commercial metal, by furnishing metal of high purity, at a reasonable price.

This review has merely touched on the commercial side of the progress in electrodeposition during the last decade. No attempt has been made to cover the enormous amount of experimental work done, which is reflected in the literature of the decade, and upon which is dependent the success of the coming decade, for we must never lose sight of the fact that the experimental process of today is the practical process of tomorrow.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, Mr. S. Skowronski in the Chair.

ELECTRODEPOSITION OF COPPER BY THE UNION MINIERE DU HAUT KATANGA.[1]

By H. Y. Eagle.

Abstract.

The new electrolytic tank house and its operation is described. Of special interest is the design of the electrolytic tanks, which are the largest of the kind ever built. The composition of the electrolyte remains uniform throughout the fifty-foot tank, and is characterized by its high acidity and consequent high conductivity. Furthermore, the temperature of the electrolyte is comparatively low (less than 40° C.) and, accordingly, the effect of iron in solution is less harmful than at the higher temperatures ordinarily employed. The energy efficiency averages 0.508 kg. Cu per kw.-hr.

During the year 1921, the Union Miniere du Haut Katanga erected at their Panda works in the Belgian Congo an experimental leaching plant for the treatment of their low-grade ores. This plant was to serve as a demonstration of the process recommended by their consulting engineer, Archer E. Wheeler, after an extended investigation of the company's ores. The general scheme of treatment was sulfuric acid leaching and recovery of the copper from the leach solution by electrolysis, but the process differs from existing leaching installations in copper metallurgy in the following particulars:

a. The process is continuous, not batch.

b. Leaching is accomplished by agitation instead of by percolation.

c. The accumulation of harmful impurities in solution is effec-

[1] Manuscript received February 15, 1924.

[2] Union Miniere du Haut Katanga, 25 Broadway, New York, N. Y.

tively controlled by a continuous treatment of part of the solution with the regular ore.

d. Electrolysis is carried out in large tank units at *slow* circulation rates.

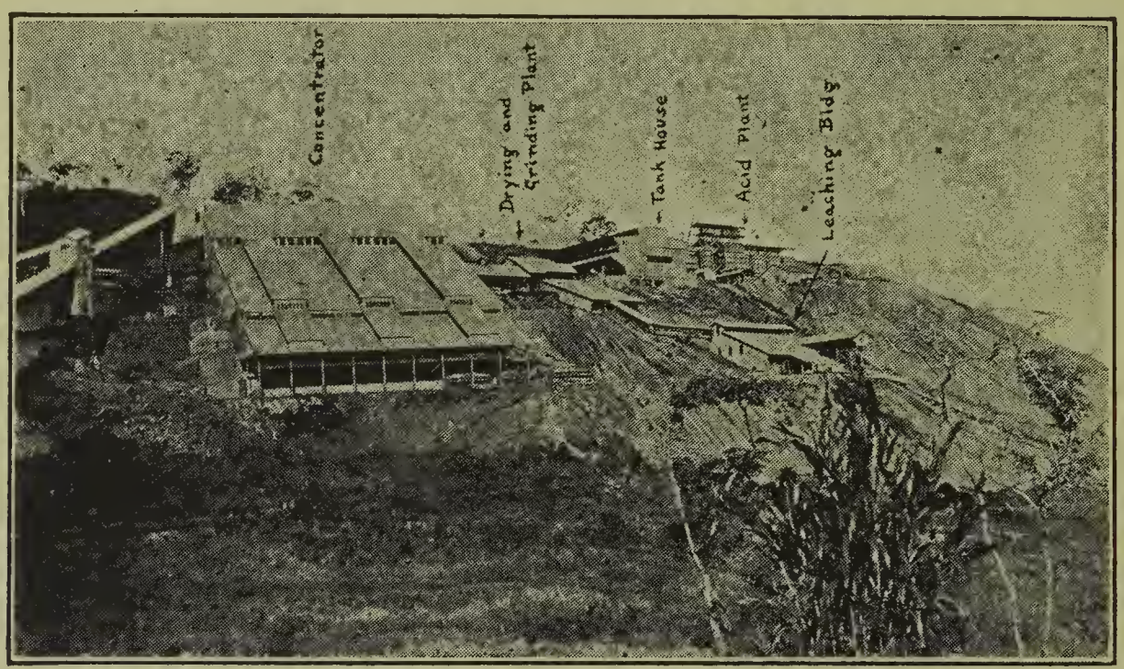

Fig. 1. General View of Leaching Plant.

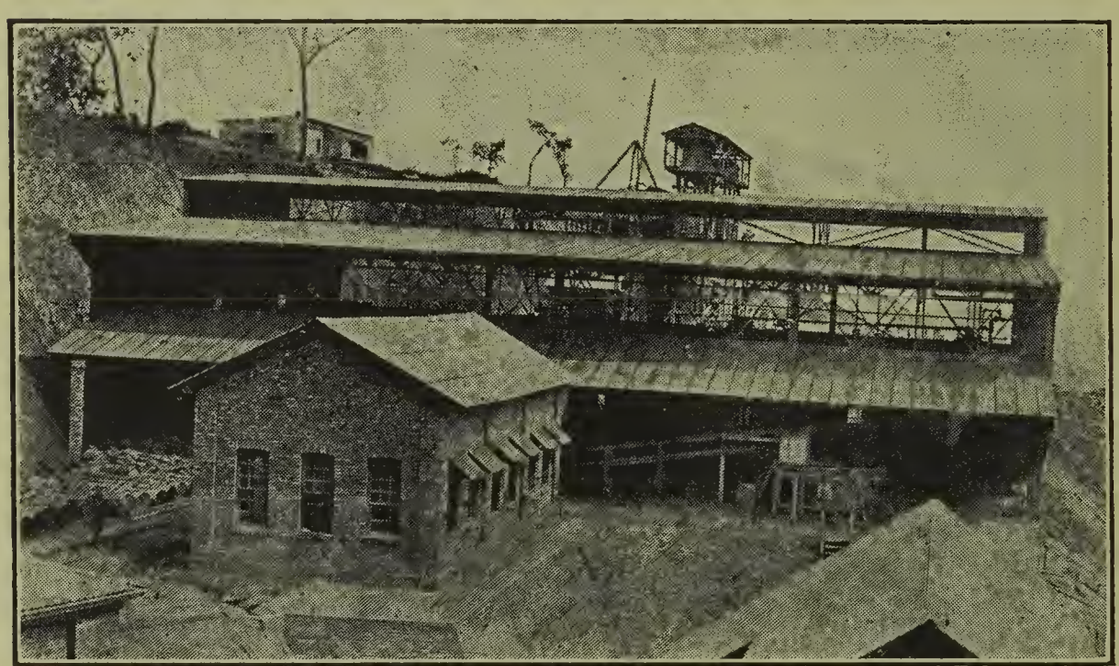

Fig. 2. Tank House. Sub-station in Foreground.

The plant has a capacity of about 100 metric tons of cathode copper per month. Operation was started on November 22, 1921, and from then until September 1, 1922, it was operated on an experimental program, under the direction of the writer, with a

view of determining the fundamental factors entering into the design of a large plant. On the first of September, 1922, the necessary data having been determined, the plant was turned over to the operating organization of the company, and has since been operated by them as a producing unit. In the following description of the electrolytic plant the results, methods of operation, etc., apply to the experimental period.

THE ELECTROLYTIC TANK HOUSE.

The electrolytic tank house, as shown in the accompanying photographs, is a steel frame structure, about 125 ft. by 67 ft. (38.5 m. x 20.5 m.) between column centers. The end walls are sheathed with corrugated asbestos, and the roof is covered with wood decking and composition roofing. The side walls are open but are protected from the weather by overhung roofs. Brick walls under the lower roof on one side enclose offices, a storeroom and the plant laboratory. The building is served by a standard 5-ton tank house crane, which handles the copper drawn from and the starting sheets charged to the tanks. A basement is provided under the tanks with ample headroom for tank inspection. Besides the above, the tank room equipment consists of six electrolytic tanks, a wash tank, unloading and stripping racks, a squaring shears, Morrow clip machine and the necessary circulation equipment.

The electrolytic tanks[3] are of considerable interest in that they are probably the largest units ever built, and from the fact that in their design advantage has been taken of a principle which has, insofar as the writer is aware, never before been recognized. It is a fact that, in an insoluble anode tank with a slow circulation rate, the composition of the solution in the tank is uniform throughout, and that this composition is the same as that of the outlet solution. This results in a tank operating at the high conductivity of the high acid outlet solution. It is obvious that the more power that can be put into a single tank, the more chemical work is done and the higher the acidity of the tank solution. This increased acidity results in a low resistance loss, which is equivalent to both decreased energy consumption and a reduction

[3] U. S. Patent 1,431,574.

in the operating temperature of the solution. This feature is of considerable importance, as it permits low circulation rates. Furthermore, the baneful influence of iron on ampere efficiency is less marked at the lower temperatures. The temperature of

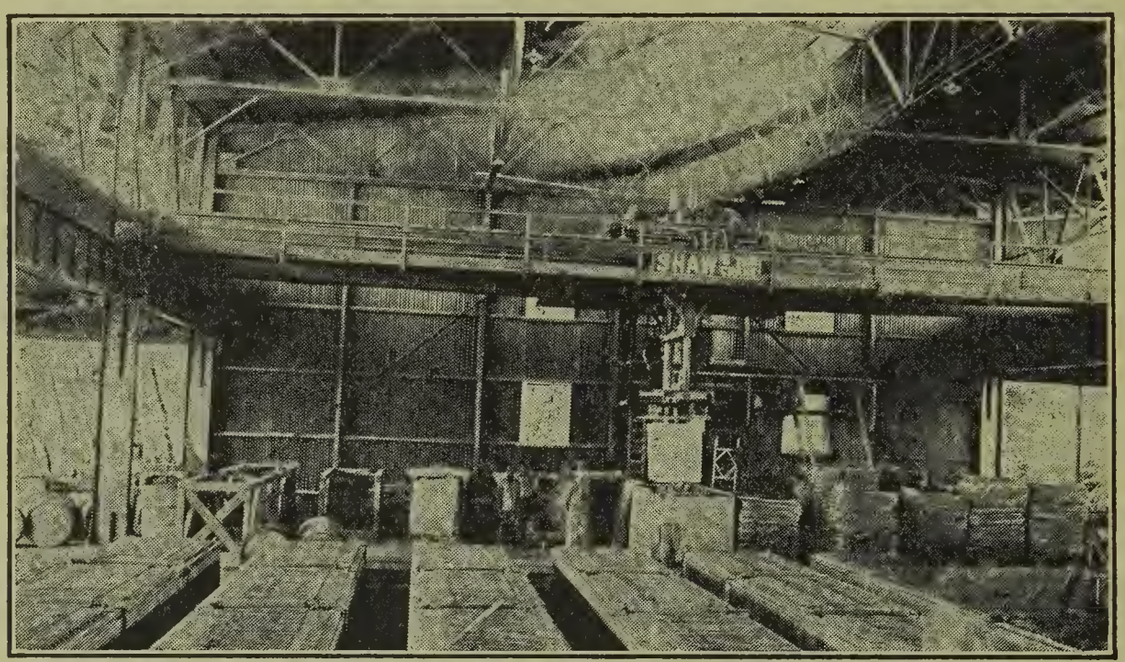

FIG. 3. Interior of Tank House from Feed End.

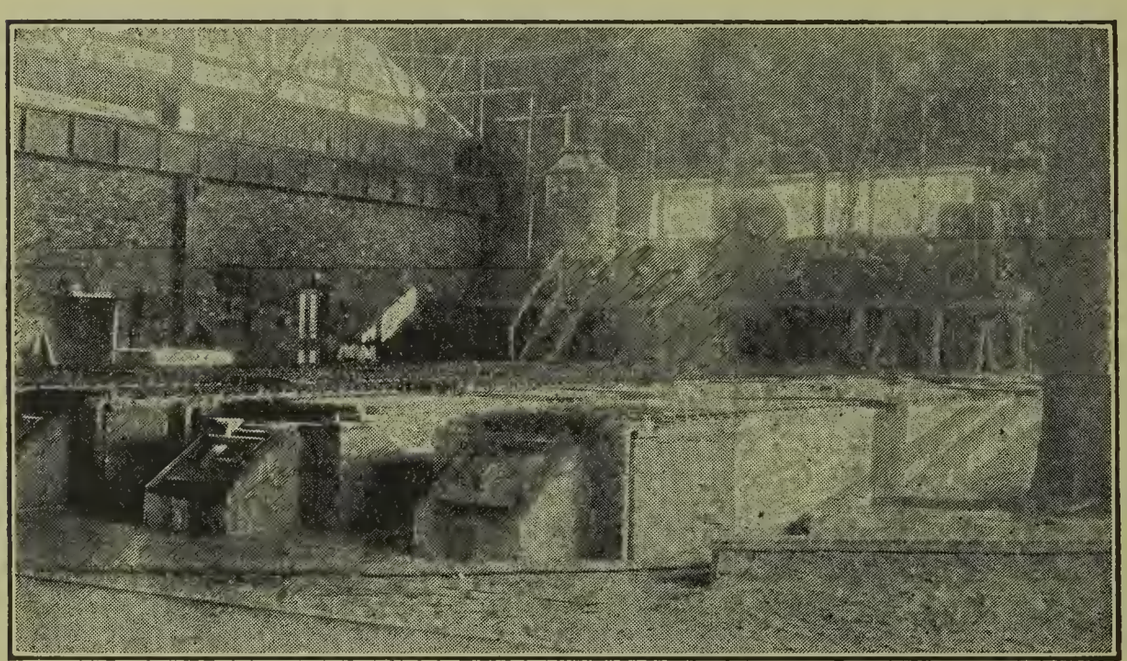

FIG. 4. Interior of Tank House from Discharge End of Tanks.

solution in our electrolytic tanks varied throughout the year with the atmospheric temperatures, but never exceeding 40° C. The difference between the inlet and outlet temperatures was less than 5° C. No addition agents were employed in the baths.

We had in mind the above facts when designing our electrolytic tanks. They are constructed of reinforced concrete, lined with 2 in. (5 cm.) of asphalt mastic, and are each of the following inside dimensions: 55 ft. 7 in. long, 3 ft. 2½ in. wide, and an average depth of 4 ft. 3 in. (17 m. x 1 m. x 1.3 m.) The electrodes are placed transverse to the tank length, and are arranged in five electrical groups in series. Each group consists of 22 cathodes and 23 anodes, arranged in multiple, and spaced at 4¾ in. (12 cm.) center to center of anodes. The electrical groups are separated from one another in the tank by a distance of about 20 in. (51 cm.) Five of the electrolytic tanks are used for the deposition of cathode copper and the other for the deposition of starting sheets. The anodes in the cathode copper tanks are of cast lead, ½ in. thick and 2 ft. 5¾ in. x 3 ft. 3½ in. (1.3 cm. x 75.6 cm. x 101 cm.) below solution line; the cathodes are stripped sheets looped on a standard Morrow clip machine, and are 2 ft. 9¼ in. wide by 3 ft. 5¼ in. deep (84.5 cm. x 104.8 cm.) The anodes in the starting sheet tank are of cast lead ½ in. thick, and 2 ft. 6¾ in. x 3 ft. 4 in. (1.3 cm. x 78 cm. x 101.6 cm.) below solution line. The cathodes are hard rolled copper starting sheet blanks, $\frac{3}{16}$ in. (5 mm.) thick, and of such size that after attaching wood strips on the edges to facilitate stripping, a starting sheet 2 ft. 9¼ in. x 3 ft. 5¼ in. (84.5 cm. x 104.8 cm.) will result.

Power is supplied to the tank house from the substation located close by, which receives power from the Panda Centrale through a 3-core armored cable. The substation contains the electrolytic motor generator set, an exciter set and necessary switching equipment, as well as a 12 in. x 10 in. (30.5 cm. x 25.4 cm.) electrically driven air compressor for supplying compressed air for pumping and agitating the solutions. Power is supplied to the tanks from a three-unit motor generator set, consisting of a 3-phase, 50-cycle, 6600 v., 750 r. p. m. synchronous motor, driving two direct current generators, each capable of delivering 3,000 amp. at a range of from 50 to 75 v. Bar lines of 1½ in. x 6 in. (3.8 cm. x 15.2 cm.) solid hard-rolled copper carry the current to the tanks, which are connected in series. The tank bars are 1½ in. x 6 in. (3.8 cm. x 15.2 cm.) solid hard-rolled copper. Thus the circuit consists of 30 groups of anodes and cathodes arranged in series, and fed by

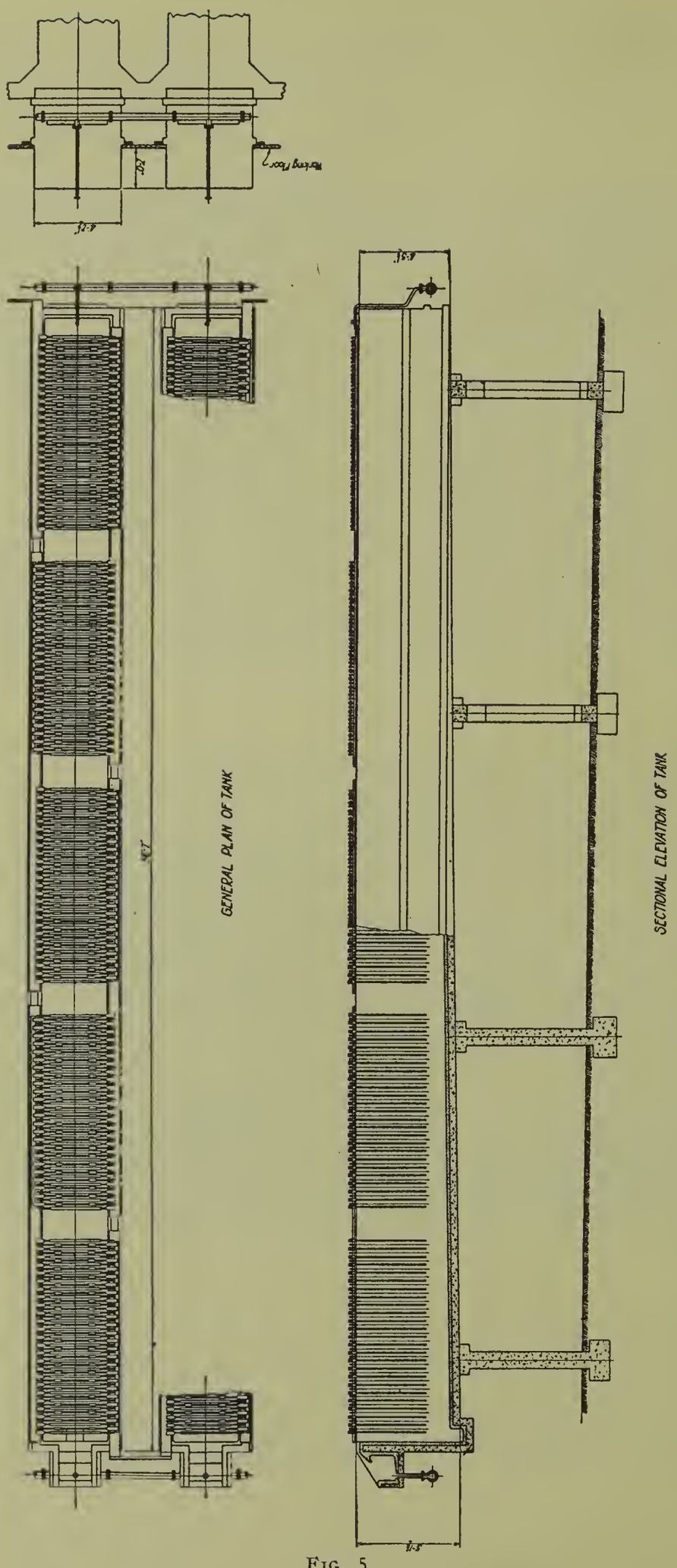

FIG. 5.

two generators operating in parallel and capable of delivering to it a maximum of 6,000 amp.

The general scheme of operation in the tank house is as follows: The high copper solution from the leaching plant is pumped, at the rate of about 100 L. per minute, to the tank house to a two-

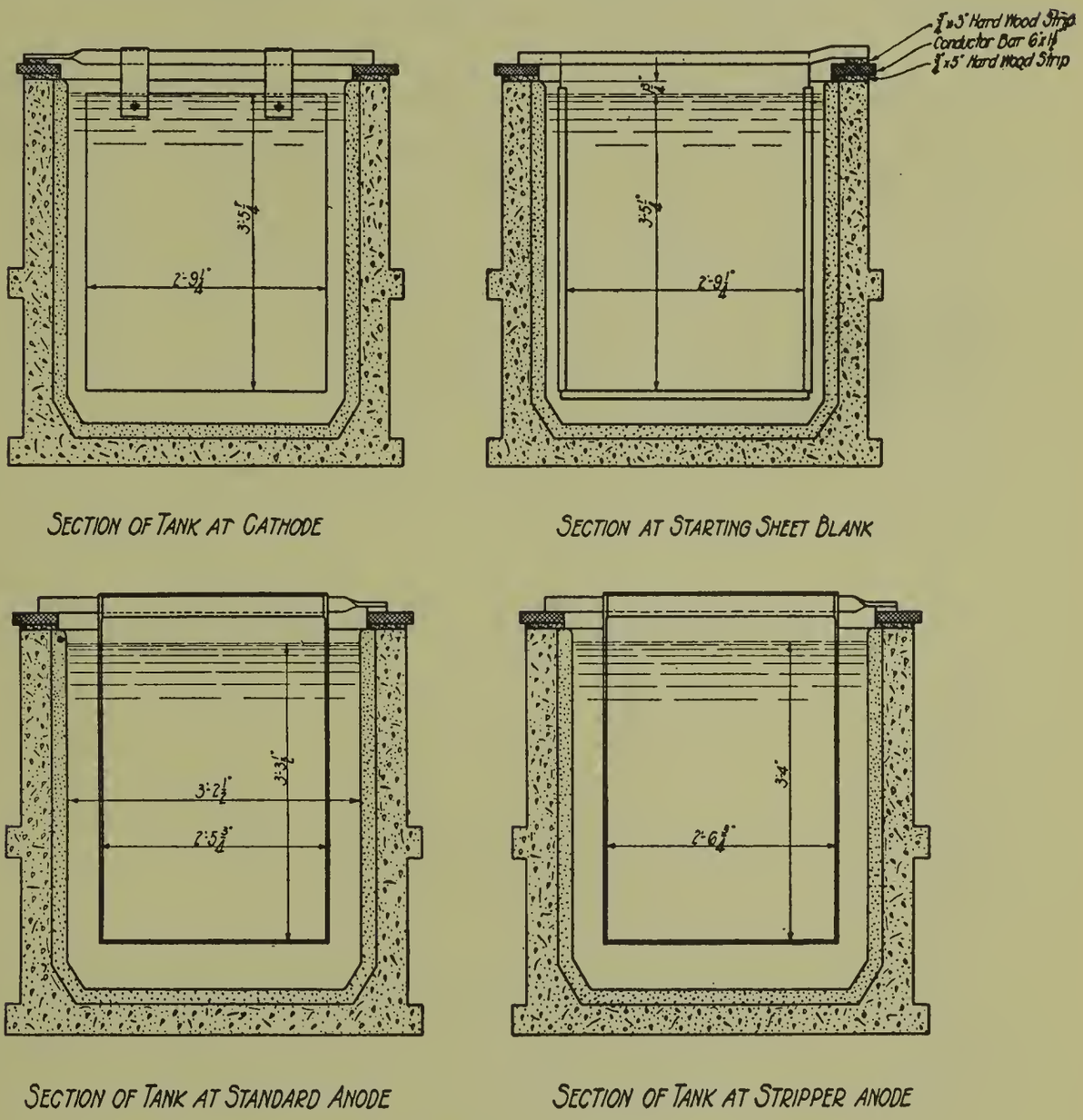
Section of Tank at Cathode
Section at Starting Sheet Blank
Section of Tank at Standard Anode
Section of Tank at Stripper anode

Fig. 6.

compartment weir box, which divides the solution into two equal parts. One of these, after having had added to it the net sulfuric acid losses encountered in the leaching, is the feed to the starting sheet tank. Starting sheets are stripped at 48 hr. intervals, and after being looped these serve as the cathodes in the cathode depositing tanks. The outlet solution from the starting sheet tank flows to a tank from which it is pumped by an airlift to

join the other half of the solution from the weir box, and this combination is divided equally into the feed to the five cathode tanks, each of which receives 20 L. per min. Copper is drawn from these tanks at from 10 to 13-day intervals. The outlet solution from the cathode tanks returns to the leaching plant, where it is again brought into contact with ore.

The starting sheet tank circulation is carried on at the higher rate (50 L. per min.) in order to cut down the variation in copper content of the solution, as it is necessary to maintain copper above a certain concentration in order to get good starting sheets. As a small range in copper content means a small amount of acid regenerated, the entire acid addition is made to the feed of the starting sheet tank to get as high an acidity and resulting conductivity as possible. The average composition of the solution is about as follows:

	Grams Per Liter	
	Solution from Leaching Plant	Return to Leaching Plant
Free H_2SO_4	15	60
Cu	35	15
Fe, total	5	5
Fe, ferrous	2	3
Fe, ferric	3	2
Al_2O_3	10	10
MgO	7	7
CaO	1	1

The total iron in our solutions was never permitted to rise above a concentration of 6.5 g. per L., and at this figure little harmful effect on ampere efficiencies was experienced. No other soluble impurities evidenced themselves in our tank house work except soluble silica, which appeared occasionally on our cathodes, particularly when changes in our methods of operation caused marked temperature changes in the tanks. Our solutions at times carried considerable slime in suspension, due to the slow settling properties of some particular ore, and some of this was mechanically entrapped in the deposited cathodes. The copper itself is of high electrolytic grade and subsequent furnace refining yields a copper of wire-bar purity.

During the experimental period we produced a total of 426 metric tons of cathode copper. The following figures are averages for the entire period and tonnage:

Cathode current density, amp. per sq. m.	98.24
Cathode current density, amp. per sq. ft.	9.13
Amp. efficiency, per cent.	83.33
Kg. Cu per kw.-hr.	0.508
Lb. Cu per kw.-hr.	1.120

Although we had no white operators who had even seen an electrolytic tank house, and a great deal of the work was done by natives, we had little trouble. The long tank did all that was hoped for, and we attribute our high energy efficiency and freedom from temperature worries entirely to its design. We did encounter one serious difficulty in starting up the plant, which may prove of interest. This arose from the fact that we could not strip starting sheets from the hard-rolled copper blanks. The sheets stuck so tight that they had to be chiselled off, and trial of all sorts of combinations of various oils and graphite yielded no results. We concluded that some condition inherent in the structure of the surface of the copper blanks was the cause of the trouble and sought means for changing it. Buffing helped, but a single amalgamation of the sheet definitely removed the trouble, and after this treatment sheets were of good structure and stripped easily.

The results of the experimental leaching plant have been such that the Union Miniere have decided to erect, in the near future, a large plant of this type at their Panda works in Katanga. Designs are being prepared for an initial unit capable of producing 30,000 metric tons of finished copper shapes per year.

DISCUSSION.

M. R. THOMPSON[4] (*Communicated*): There is one important point in this paper not fully explained. The author states, on page 367: "The composition of the solution in the tank is uniform throughout, and that this composition is the same as that of the outlet solution." On page 372,

[4] Chemist, Bureau of Standards, Washington, D. C.

however, it is shown that the copper content of the inlet solution is 35 g./L. and that of the outlet is 15 g./L. It is not stated nor shown in the paper just how, with such a difference in composition, a concentration gradient in some direction, longitudinally, transversely or vertically, is avoided. The patent mentioned, however, provides for auxiliary feeding of strong copper solution along the side of the tank at each section, in addition to the feed at the inlet end, also for the use of baffle plates between sections. Such devices reduce the concentration gradient in one direction or another, and also the difference in composition between the inlet and outlet solution. Usually, in an insoluble anode tank the concentration gradient is greater the slower the circulation rate, and at Katanga the latter is relatively very slow compared with the tank volume. At a flow of twenty liters per minute, it would apparently require about 17 hr. to displace the entire contents of a tank.

According to C. W. Eichrodt,[5] with present practice at Chuquicamata the contents of a 16-tank section are displaced every 3 hours, or at the rate of about 11 minutes per tank. This is relatively very rapid circulation. If these data are correctly interpreted, the difference in copper concentration between inflow and outflow of a single tank is only about 0.4 g./L., hence solution samples from various parts of a tank would scarcely show a noticeable variation, and only a small concentration gradient could exist. Conditions in the Chuquicamata tank are, therefore, too widely different from those at Katanga to furnish a good comparison with the latter tank.

Points of considerable interest to tank house operators are: Omission of mention of any oil cover being required on top of the tanks to keep down acid spray; the regular and successful production of starting sheets in the insoluble anode tanks, which has usually been regarded as a difficult feat, and the familiar difficulties of "breaking-in" new copper starting sheet blanks. Amalgamation, as described, is an excellent treatment, but either to supplement it or without it, special grease formulas have been used temporarily at such times with good results. The increased cost during an emergency is usually warranted, until the plates are in such good stripping condition as to permit the substitution and

[5] This volume, page 381.

regular use of a cheap grease or oil. Animal fat seems to give an especially good separation. Hot, fluid mixtures of tallow, lard and rosin have been used and found to be very effective, but are more readily applied mechanically than by hand. The efficiency of such mixtures seems to increase, within certain limits, as the percentage of lard used is increased.

COLIN G. FINK[6]: It is this long tank or long electrolytic cell at Katanga which in one way distinguishes the process from the process employed at Chuquicamata, Chile. As Mr. Eagle put it, "I can only tell you what I actually found," and the feed to this long tank is such that at any cross-section, at any part of that long tank the concentration is practically the same. Say we take a pipette and lower it 10 cm. below the surface, we will get samples which show the same analysis at any part of this long tank. That is to say, the concentration drop is very steep and vertical and not a gradual slope as you might expect. Of course, the solution leaving the tank leaves it at 15 g. per L. and enters at 35 g., but very close to the feed the concentration is practically 15 grams.

CARL HERING[7]: Then the average is 15 and not 35, according to your explanation.

ALFRED STANSFIELD[8]: At first I found it difficult to believe that the solution could have a uniform composition throughout the long electrolytic tanks. Later I realized that the incoming solution, being heavier than the partly exhausted solution, passes downwards on entering the tank and flows along the bottom so as to form a nearly uniform layer of rich solution. The bubbles of gas rising between the electrodes cause an upward mixing of the richer solution all over the tank, so that the composition of the electrolyte, taken at equal depths from the surface, is the same throughout the tank.

COLIN G. FINK: The feed is from the top and the outflow from the top too, which is contrary to some practice. The heavy solution sinks, just as Prof. Stansfield points out, and due to the gas circulation it is rapidly mixed with the rest of the solution. The

[6] Head, Division of Electrochemistry, Columbia Univ., New York City.
[7] Consulting Elec. Engr., Philadelphia, Pa.
[8] Prof. of Metallurgy, McGill Univ.. Montreal. Canada.

term "throughout" is perhaps a little overdrawn. If a chemist had a very long pipette he would find a difference in concentration, depending upon the length of his pipette.

ALFRED STANSFIELD: Could Mr. Eagle give us any information as to the amount of leakage that takes place between the different batches of anodes and cathodes?

A. L. FERGUSON[9]: I am not familiar with the commercial application to any great extent, but it seems to me that you would get an extensive local action under these conditions. If you have such a highly concentrated solution at the bottom and low concentration at the top, a concentration cell effect will be developed, which would result in unequal distribution of current, as well as local action between the top and bottom of the plater.

S. SKOWRONSKI[10]: That was the very point I tried to bring out at first. Undoubtedly the author must get different efficiency at different levels in the tank.

COLIN G. FINK: Mr. Skowronski says that you should get differences in efficiency because there are differences in the copper concentration at different levels. Do not forget that we are dealing with an insoluble anode process here and generating sulfuric acid. We are reducing the conductivity by depleting the solution in copper. But we are far more increasing its conductivity by increasing the sulfuric acid content, and we are operating within a close range, 35 to 15 copper. The difference in the appearance and quality of the cathode sheets from the top to the bottom is practically nil.

E. J. JORGENSEN[11]: I want to quote a few facts from actual practice. In Chuquicamata I had samples withdrawn from an electrolytic tank about 20 ft. (6.1 m.) long, holding cathodes 4 x 3 ft. (1.22 x 0.92 m.). Samples near the top, half way down, and at the bottom showed the same result in several vertical cross-sections through the length of the tank. This permitted the removal of special arrangements to draw the solution from the bottom of one tank to the top of the next. I have several other proofs that the gas generated on an insoluble anode gives excellent circulation.

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[10] Research Chemist, Raritan Copper Wks., Anaconda Copper Co., Perth Amboy, N. J.
[11] Irvington Smelting and Refining Works, Irvington, N. J.

T. B. HINE[12]: This question about breaking in the starting sheets interests me from the standpoint of metal adherence. As Mr. Thompson has spoken about amalgamation and the use of oils, some of you who have had experience with it might say whether this amalgamation is a customary procedure or not.

S. SKOWRONSKI: In the last few years, all the refineries have adopted amalgamation as a method of breaking in new blanks. Formerly it was a long and tedious task to break in blanks, repeated application of asphalt paint being necessary and the sheets for the first week, and sometimes longer, could not be used. The trouble was due to the fact that the copper deposit would follow the crystal structure of the rolled copper and adhere fast to the blank. This is now overcome by amalgamation of the surface of the blank. While metallic mercury may be used, a solution of mercury in an excess of nitric acid works more quickly, and is more easily applied. Only one application of mercury is usually necessary, the first sheet is always good, and after the first deposit the blank is "broken in" and red engine oil, or other oils, may then be used, to prevent the deposited copper from sticking fast to the blank.

This is a good example of the effect of the crystals of the metal forming the cathode upon the crystal structure of the deposit. This subject has been recently discussed at length in this society. In our case continuity of crystals is not desirable, and mercury acts as the intervening metal, to break up the crystal structure.

T. B. HINE: I have noticed at the Western Electric Co.'s plant in the electrolytic iron work where we grease iron sheets with mineral oil, there is a certain amount of formation of channels. It looks as though the oil had come out in little channels through the iron. There are oxide deposits in these channels. I wonder whether in other metal deposition that same sort of pitting or hole formation occurs.

S. SKOWRONSKI: In greasing starting blanks, precaution must be taken to use as little oil as possible. The thinner the film of oil, the better, provided of course the blank is completely covered. Uniformity of the thickness of the oil deposit is the essential

[12] Research Chemist, Western Electric Co., Hawthorne, Ill.

factor, for otherwise the copper will not plate out uniformly on the blank and the resulting sheet will be what is called "lacey" in character. That is, it will be so full of holes and thin in spots that it will resemble a piece of lace.

C. S. WITHERELL[13] (*Communicated*): A concentration gradient which Mr. Thompson has shown must exist, may be explained as follows: The inflow solution being of higher specific gravity than that within the tank tends naturally to sink to the bottom and form a stratum beneath the electrodes. The solution rising from this stratum would have a sharp drop in concentration gradient in a narrow transition zone at the bottom edges of the electrodes, this zone perhaps not being over several inches in depth. Above the zone mentioned, the stirring effect of the anode gas and convection currents caused by ohmic heating would maintain the main body of the solution at a nearly uniform concentration. There would still necessarily remain a slight concentration gradient in a vertical direction, as well as longitudinally in the tank, due to the general drift of the electrolyte from inflow to outflow. Very careful spot sampling of the electrolyte would be required to demonstrate the conditions described.

H. Y. EAGLE (*Communicated*): I observed, while employed in the Great Falls electrolytic plant, that the composition of the solution in our liberating tanks, or the cells in which the copper was being electrolytically deposited, was apparently uniform throughout the tank, and was the same as that of the outlet solution. The word "throughout" is not intended to be overdrawn as Dr. Fink suggests, but means what it says—same at any level and at any position in the length of the tank—no vertical gradient and no horizontal gradient. It was surprising to find that this was so, but if true in a tank 10 feet 3 inches long, why not so in one 50 feet long? If it were true when thus extended the power savings were worth money and accordingly the idea was patented. The Katanga work offered an opportunity to test the phenomenon out on long tanks, and the same conditions were found to exist. The explanation of this phenomenon lies undoubtedly in the tremendous internal circulation set up by the gas evolution. From observations made, I estimate that this inter-

[13] Metallurgical Engineer, New York City.

nal circulation is probably more than 500 times as effective as the circulation due to feed of new solution. A condition such as this leaves little room for any gradient in solution assay.

I would suggest to any of our members whose credulity is too severely strained by the idea, that it would be easy for those engaged in electrolyte cell room work to test it out themselves in their own liberating tanks, or have some friend in the plant do it for them.

Regarding electrical leakage between adjacent groups in a tank, this is very small. Our practice was to hang an anode insulated at both ends of its bar, at the ends of each group. This effectively screened any electrical leakage as is best evidenced by our energy efficiencies.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, Mr. S. Skowronski in the Chair.

THE ELECTROLYTIC TANK HOUSE, CHILE EXPLORATION COMPANY, CHUQUICAMATA, CHILE.[1]

By C. W. Eichrodt.[2]

Abstract.

The natural copper sulfate mineral is leached with spent electrolyte. The strong solution, high in copper and low in sulfuric acid, is treated with finely divided copper to remove the chloride ions as cuprous chloride. After dilution of this strong solution with solution partly electrolyzed, it passes into the electrolytic tanks. These tanks are constructed of concrete, and are lined with acid-proof mastic. At the rate of 800 L. per min. the solution passes through a 16-tank section in less than 3 hr. With the introduction of the new copper silicide (Chilex) anode and the new plating-down chloride precipitation process the acid plant and cooling tower have been dispensed with, and the iron content of the electrolyte has been reduced from 20 g. down to about 3 g. per L. The marketable cathode copper is of an average purity of 99.96 per cent Cu. The conductivity of the annealed metal is 100.9 per cent of the Mathiessen standard. Details of tank house operation are given, including complete analyses of electrolyte, starting sheet manufacture, mechanical handling of the copper, proper spacing of electrodes and electrical equipment.

[C. G. F.]

GENERAL ARRANGEMENT.

At present there are eight electrical tank circuits in the house. The number of tanks per circuit varies from 96 to 164. In all circuits the tanks are in series, and in all tanks the electrodes are in multiple. There are 894 tanks in the house. For the purpose

[1] Manuscript received February 12, 1924.

[2] Chile Exploration Co., Chuquicamata, Chile.

of circulation, the tanks are arranged in sections; the standard section consisting of 16 tanks. There are, however, also 3 ten-tank sections. A section is a cascade of tanks so placed, that the outflow of one tank forms the inflow of the succeeding. The general direction of flow through each individual tank is perpendicular to the electrodes. The tanks are 18 feet 8 in. by 3 ft. 5 in. and 5 ft. 10 in. deep (569 x 104 x 178 cm.) inside dimensions. They are of reinforced concrete with mastic lining, and are referred to in more detail near the end of this paper.

The electrolytic tanks may be further considered in three classifications, starting sheet tanks, plating down tanks, and commercial tanks. Four 16-tank sections are utilized for the production of starting sheets, two 10-tank sections for "plating down" (partial depositing out of copper) that portion of the leaching solutions to be discarded, and the balance of the tanks for extracting copper from the strong solution produced by the leaching of the ore. The last mentioned are termed commercial tanks, and the electrolyte therein treated, commercial solution. Strong solution is reduced to spent electrolyte (the solution which is returned to the leaching plant for enrichment) in two stages. From 12 to 18 sections, 24 to 36 per cent of the commercial house, are used on second stage deposition, and the remainder on first stage.

A separate electrolyte is used in the starting sheet sections. This is a pure acid copper sulfate solution, perpetuated by the soluble copper anodes used, and circulated in a separate closed circuit. The soluble anodes used for the production of starting sheets are made from secondary copper produced in the dechloridizing plant and smelter, plus a portion of the commercial cathodes. The anode spacing is 5 in. (12.7 cm.) and there are 43 anodes and 42 starting sheet blanks per tank. Both copper and lead blanks are in service, about 80 per cent being copper. These blanks produce a sheet 37 in. by 50 in. (94 cm. x 127 cm.), giving an effective cathode area of about 24 sq.ft.(0.22 sq. m.).

In the plating down and commercial sections, the insoluble "Chilex" anode is used. The spacing used for insoluble anodes is 4.5 in. (11.4 cm.), at which spacing there are 50 anodes and 49 cathodes per tank.

Formerly the leaching solutions to be discarded were completely deposited out in the electrolytic tank house. Exceedingly poor

current efficiencies and cathodes of impure copper, fit only for secondary copper, were obtained in this process. The solutions to be discarded are now merely "plated down" (reduced to a copper content of from 8 to 10 g./L.) in the electrolytic tanks, and the process of extracting the copper completed in the dechloridizing plant. The "plated down" solution from the electrolytic cells used for this purpose is returned to the wash agitators in the dechloridizing plant, where it is mixed with excess cement sopper and $FeCl_2$ solution. The copper is precipitated according to the following reaction:

$$Cu + FeCl_2 + CuSO_4 = Cu_2Cl_2 + FeSO_4$$

Excess cement copper is used, so that the solid product that settles out is a mixture of cement copper and cuprous chloride. This mixture is known as washed cement copper, and is used for dechloridizing the strong solution for the tank house. After the reaction, the solution is decanted off and goes to waste. This process has the following advantages over the old depositing out process. (1) The "plating down" cathodes are sufficiently pure for the wire bar furnace, and the secondary copper is supplied by the excess cement copper now produced in the dechloridizing plant. This results in greater flexibility of operation. (2) The capacity of the tank house has been considerably increased for the preceding reason and for the additional fact that the current efficiency obtained in "plating down" is far higher than that obtained in "depositing out" and fewer tanks are required in the "plating down" process. (3) There is less iron in the "washed cement" copper than in the cement copper used before the "plating-down precipitation" process was introduced. Hence less iron is now introduced into the commercial solution in dechloridizing.

CIRCULATION AND THE COMMERCIAL ELECTROLYTE.

The strong solution (the first product from treatment of the ore) is sent to the dechloridizing plant. Here the chlorine is precipitated from the solution as Cu_2Cl_2 by cement copper. The cement copper also serves to reduce the ferric iron to ferrous. The dechloridized solution passes through settling tanks for removal of the suspended Cu_2Cl_2 and cement copper, and is pumped to the tank house first stage head tank. After dechlorid-

izing, the solution contains from 40 to 60 g. per L. in copper. Dilution with electrolyzed solution reduces the copper content to an amount suitable for first stage inflow. These electrolyzed solutions contain ferric iron. Hence the commercial solution even in the stage of first stage inflow, contains ferric iron.

The first stage commercial sections are fed by gravity from the head tank. Part of the outflow from these sections is returned to the first stage head tank for mixing with the strong solution,

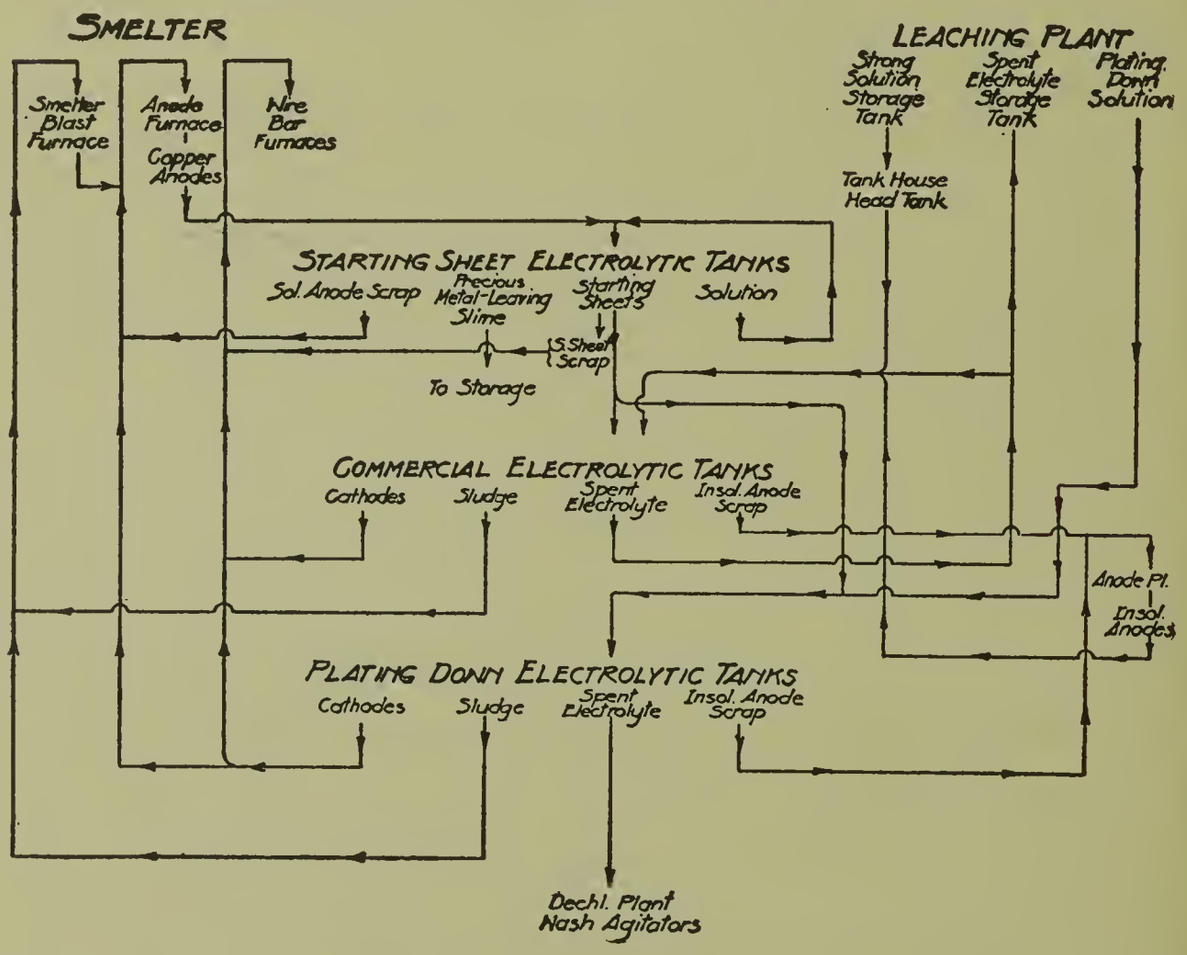

FIG. 1. Flow Sheet of Electrolytic Tank House.

and the balance pumped to the second stage head tank. The second stage head tank feeds the second stage sections by gravity, and the outflow from the tanks (spent electrolyte) is returned either to the head tank, or to the leaching plant, as the conditions may require.

All pipe lines are now of wood stave. The gravity feed system from the head tanks consists of 24 in. (61 cm.) main pipe lines, 12 in. (30.5 cm.) arteries and 4.5 in. (11.4 cm.) branches from the arteries to the individual sections. The outflow from the sec-

tions is conducted to the pump house by a system of reinforced mastic canals. In the pump house, Worthington 15 in. (38 cm.) vertical centrifugal pumps, driven by 200 h.p. motors, are used for returning the solution to the head tanks and leaching plant. The pump deliveries are 15 in. (38 cm.) wood stave pipe.

An analysis of the monthly composite of spent electrolyte for October, 1923, is tabulated below.

Sp. Gravity	1.175
	g./L.
Cu	14.2
Cl	0.43
Fe	4.2
SO_4	171.3
HNO_3	10.38
Al	1.65
As	0.188
Sb	0.028
Ca	0.68
	g./L.
Mg	3.10
Na	19.05
K	2.63
Pb	0.018
Sn	0.025
Mn	0.061
Total Solids	213.13
Total Acidity	83.3
Total H_2SO_4	72.9

The practice in regulating the circulation is to fix on the copper content of the spent electrolyte. It is desired to maintain this at 15 g. per L. Below this point, it has been found that the current efficiency is decreased. The copper is extracted to 15 g. per L., because as much free acid as possible, up to the limits explained later, is desired for leaching. With this in view, the copper content of the inflows is regulated to meet the load requirements. It is possible to regulate the rate of flow in the individual sections, but as a rule, the maximum flow of about 800 L. per min. per section is maintained throughout the house. A rapid flow aids in the production of a smooth deposit of copper. It also gives a high solution level in the tanks, thereby keeping down the current density. In fact, the flow is usually kept up to the maximum rate that can be passed through the tanks without danger of submerging the anodes.

At the rate of 800 L. per min., the solution passes through a 16-tank section in a fraction less than 3 hr. Hence the time interval between first stage inflow and second stage outflow, or spent electrolyte, is about 6 hr. In passing through 16 tanks, approximately 0.45 g. per L. per unit of current density is extracted from the electrolyte. With the present average load of 28,000 kw. on the house, first stage inflow is maintained at about 27 g. per L. Cu and the second stage at 21 g. per L. Cu.

The content of the commercial solution tends to vary with the constituents of the ore treated, and is controlled by the proportion of spent electrolyte bled off for discard. An upper limit of 90 g. per L. total free acid has heretofore been set for the spent electrolyte, as above this limit the increase of undesirable impurities dissolved from the ore seems to increase considerably. The

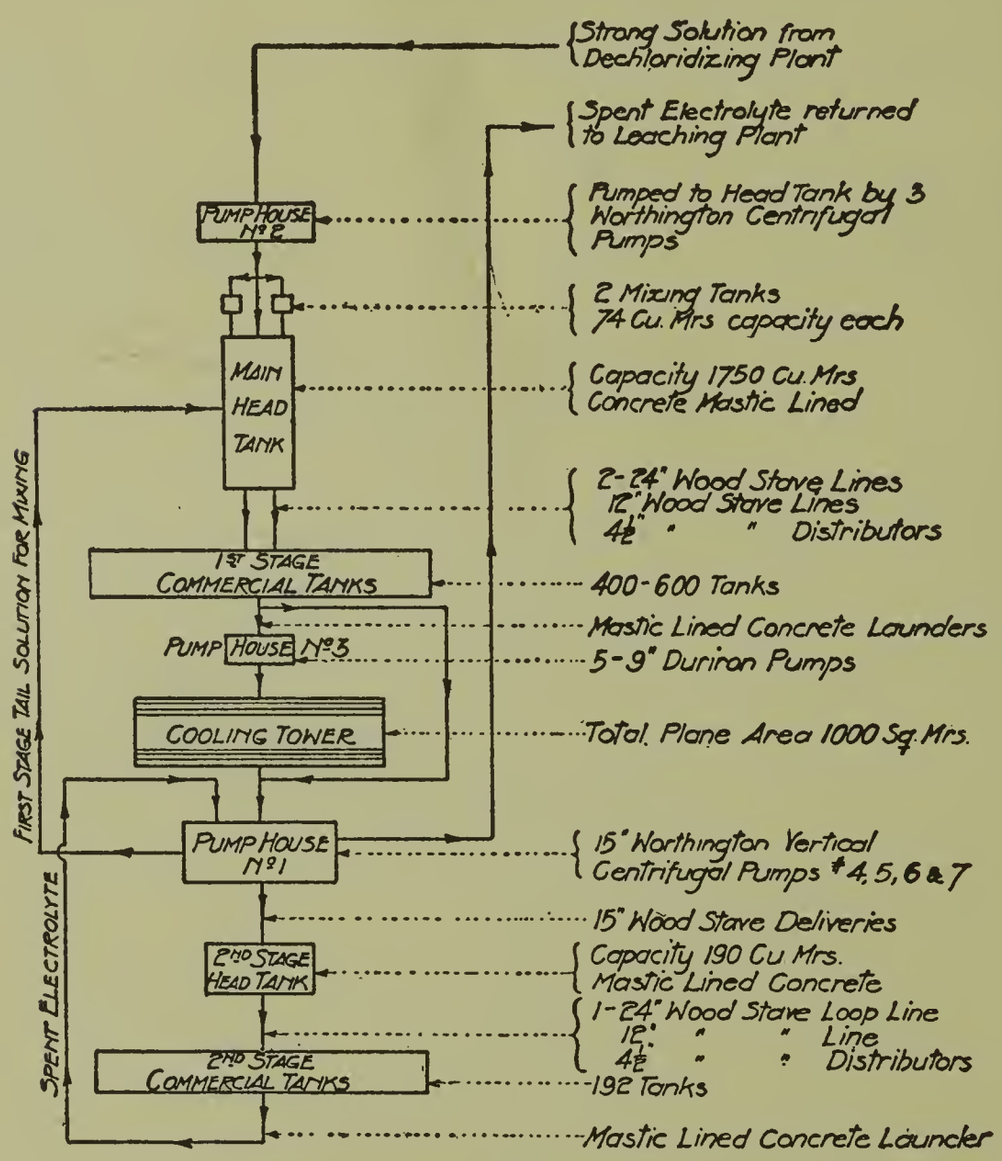
Strong Solution from Dechloridizing Plant
Spent Electrolyte returned to Leaching Plant
PUMP HOUSE No 2
Pumped to Head Tank by 3 Worthington Centrifugal Pumps
2 Mixing Tanks 74 Cu. Mrs capacity each
MAIN HEAD TANK
Capacity 1750 Cu. Mrs Concrete Mastic Lined
2-24" Wood Stave Lines
12" Wood Stave Lines
4½" " " Distributors
1st STAGE COMMERCIAL TANKS
400-600 Tanks
Mastic Lined Concrete Launders
PUMP HOUSE No 3
5-9" Duriron Pumps
COOLING TOWER
Total Plane Area 1000 Sq. Mrs.
FIRST STAGE TAIL SOLUTION FOR MIXING
PUMP HOUSE No 1
15" Worthington Vertical Centrifugal Pumps #4, 5, 6 & 7
15" Wood Stave Deliveries
SPENT ELECTROLYTE
2nd STAGE HEAD TANK
Capacity 190 Cu Mrs. Mastic Lined Concrete
1-24" Wood Stave Loop Line
12" " " Line
4½" " " Distributors
2nd STAGE COMMERCIAL TANKS
192 Tanks
Mastic Lined Concrete Launder

FIG. 2. Flow Sheet of Commercial Solution.

conductivity of the electrolyte increases with the free acid concentration. Furthermore, the voltage variation with acid content of the electrolyte is in excess of the amount that would be expected from the conductivity change. Free acid in the solutions evidently plays a double role, affecting the transfer resistance, polarization or over-voltage, in addition to the resistance of the electrolyte.

A conclusive study of the effect of acidity has not been made, and the economical acidity has been determined from the results of operation of the entire plant. It is quite probable that recent changes in conditions, and especially with the introduction of the new anode, the acidity of the electrolyte may be raised. Experiments to determine the advisability of this are now being conducted. Another danger attending the increase of total acidity, lies in the fact that the nitric acid will probably increase in the same ratio as the total acidity. Since the first year or so that the tank house has been in operation, the nitric acid content of the solutions has been kept as low as possible. During the period of high nitric acid the *cathodes* were badly corroded.

With 80 to 90 g. per L. acid a very small amount of iron is picked up by the solution from the ore. Iron is introduced in the dechloridizing process by the cement copper. A second wash of this copper, which will free it of the iron, will soon be installed. Formerly, the bulk of the iron came from the ferro-silicon anodes, and at one time the iron content of the electrolyte rose to 26 g. per L. with disastrous results.

As long as the ferro-silicon anodes were in use, in order to keep the iron below 20 g. per L., it was necessary to discard spent electrolyte almost entirely, and to add acid to the leaching solutions. This necessitated the operation of the acid plant, and the iron content of the solution indicated a balance between the cost of acid, and the cost of power lost by decreased current efficiency. Since the introduction of the Chilex anode, the iron has been gradually reduced to its present amount. With the second wash of the cement copper and gradual replacement of the spent electrolyte, it is expected that the iron will drop to less than 3 g. per L. in the commercial solution.

The amount of ferric iron is considered of more direct importance than the total iron and is not necessarily in proportion thereto. Formerly, with the total iron as high as 20 g. per L., the amount of ferric iron seldom rose to more than 3 g. per L., while at 4 g. per L. total iron, the ferric iron averages about 1 g. per L. On the whole, the proportion of ferric to total iron is higher with the Chilex anode than with the ferro-silicon. This point is of importance in consideration of the comparative volt-

ages, as well as of current efficiencies. However, the proportion varies even with the same anode, and often without any apparently significant changes in conditions.

In passing through a section, the iron may be oxidized, subsequently reduced, when it attacks the cathodes, reoxidized and again reduced. It is impossible to determine how many times iron changes state, or what portion of the iron does change state. Analyses of the electrolyte, sampled as it passes from tank to tank, show irregular increases and decreases of ferric iron, but generally show an average increase. There is no assurance that corrosion of the copper will be minimized by a reduction of all the iron to the ferrous state in the inflows. A series of experiments was recently conducted, in which the inflow to an individual section was agitated with cement copper until the ferric iron was completely reduced. It was found that a considerable portion of the iron was reoxidized in the first tank, and that this portion did not increase materially throughout the rest of the cascade. If ferric iron attacks the cathodes, and it undoubtedly does, the rate of reduction to the ferrous state, through this reaction, must just about balance the rate of oxidation of the iron, after a certain amount of ferric iron is once formed. The corrosion of the cathodes might have been retarded in the experiment, but probably not to any great extent.

To positively prevent ferric iron from attacking the cathodes would necessitate suppression of the oxidation of the iron, or, introduction of some other material, with which the ferric iron would more readily react. It may be that very fine cement copper or Cu_2Cl_2 suspended in the electrolyte as it passes through the tanks, will effect the desired result. This observation is based on the fact that the periods when the tank house has been drawing very heavy flows of solution from the dechloridizing plant, and the settling conditions have been poor, have corresponded to periods of comparatively excellent current efficiencies. While this may have been merely coincidence, the matter is now being given close attention, and whenever Cu_2Cl_2 and cement copper stock is excessive, suspended material in the dechloridizing solution is permitted to go to the tank house in considerable quantities.

The other constituents of the solution are considered of rela-

tive unimportance, although it is of distinct advantage, with regard to voltage, to keep down the total SO_4 and solids.

In passing through a section under normal operating conditions, the temperature of the electrolyte rises about 0.8° C. per gram per liter of copper extracted. At the present full load of about 28,000 kw., and with full flow of 800 L. per min., the average temperature rise in each stage is about 4° C. The temperature of the solution in passing from first stage inflow to second stage outflow is increased by about 7° C., there being some cooling while circulating between stages. No use of cooling towers is made at present and the temperatures are permitted to rise until the cooling effects due to the inflow of strong solution from the dechloridizing plant and the radiation in the head tanks, balance the heating effect of the current. This balance changes with the seasonal variation of atmospheric temperature, and the average temperature of the electrolyte, when thus allowed to come to normal adjustment, will vary between 30° and 40° C.

For the Chilex anode, the voltage temperature relation is approximately expressed by the following equation:

$$VI = Vo - (34\text{-}T1)\ D/10$$

where VI = Voltage at temperature T1; Vo = Voltage at temperature 34° C., and D = Current Density at 4.5 in. (11.4 cm.) spacing.

As is the case with acidity, temperature variation affects the voltage more than would be expected if the conductivity of the electrolyte were the only factor affected. This is true for the ferro-silicon anode as well as the Chilex anode, the former being a trifle more sensitive to temperature than the latter.

When the ferro-silicon anode was in use, and even with the Chilex anode before the iron content of the electrolyte had been reduced to very near 4 g. per L., it was found that the current efficiency began to decrease considerably whenever the electrolyte temperature rose above 28° C. With the iron from 15 to 20 g. per L., and with the ferro-silicon anode, the most economical temperature, which is determined by consideration of both voltage and current efficiency, was about 31° C. Under these conditions, the solutions were passed over cooling towers before returning to the head tanks. After the change in anodes the economical tem-

perature rose as the iron dropped, until it passed the natural temperature balance, previously explained. Hence the cooling towers have been abandoned and no further need of them is now contemplated.

THE CHILEX ANODE.

The following is quoted from a report by Charles L. Burdick: "The Chilex anode consists essentially of an alloy of copper, silicon, iron and lead. In addition it has been found that a small amount of tin is beneficial, and for a time it was believed that the presence of about 4 per cent of manganese was desirable. On microscopic examination of etched specimens, the anode is seen to consist of two main constituents, one substance separated in primary crystals and very resistant to corrosion, and the other a binary or ternary eutectic mixture much more readily corroded. The primary crystals consist of free silicon, and the eutectic carries the rest including the lead and tin."

"The behavior of the anode is similar to that of a storage battery plate. The latter consists of lead peroxide particles, which serve as current conductors to the solution, embedded in metallic lead, which serves as metallic conductor and current distributor and as the supporting grid to give mechanical strength. In the Chilex anode the eutectic has the same function as the lead peroxide produced from the lead in it by the oxidizing action of the current. The free silicon is the supporting grid and serves to protect the anode against too rapid mechanical and chemical corrosion."

STARTING SHEET PRACTICE.

The standard to which the tank house strives to keep the starting sheet solution is as follows:

Temperature	40 to 45° C.
Copper	35 to 40 g. per L.
H_2SO_4	100 g. per L.
Chlorine	0.035 g. per L.

All other constituents as low as possible.

As previously mentioned, this electrolyte is perpetuated by the copper anodes. However, unless underpoled copper anodes are used, there is a tendency for the copper content of the solution

to drop. With underpoled anodes the copper rises. The above statements are true, as a rule, but due to complications of other conditions, the control of the copper content is not so simple. Whenever this tendency is exhibited, the general practice in Chuquicamata is to take advantage of the copper increase, by making blue stone, which is kept as a reserve in case of emergency, or more frequently, by plating down in one tank with lead blanks substituted for the anodes. The latter process aids in keeping up the acidity of the electrolyte, and is a much cheaper method of accomplishing this result than that of adding commercial H_2SO_4.

The preceding statement is based on calculations and data from actual operations. It is necessary, however, in addition to the acid formed by plating down, to add about 5 tons of commercial acid per month. To keep the temperatures as desired, it is sometimes necessary to introduce steam into the solution. The chlorine content is maintained by the addition of salt. To a total volume of 500 cubic meters of starting sheet solution, 2.5 kg. of glue are added per day.

To produce in 24 hr. sheets of the desired weight (about 13 lb. or 6 kg.) a load of 19,600 amp. is maintained on the starting sheet tanks. A 6 kg. sheet is about 1/32 in. (0.8 mm.) thick. The load mentioned gives a density of 17.8 amp. per sq. ft. (1.9 amp./sq. dm.) on the blanks. To avoid unduly high density while the deposit is very light, the blanks from half of every tank in the four sections are stripped. This gives at least a four-hour deposit on any of the blanks before they are subjected to the doubled density. With this system it is not necessary to reduce the load while stripping, as was formely the practice.

With all four sections in service, 5376 sheets are produced daily. This is a fraction more than needed for full production, and permits of an occasional shutting down of a section for cleaning or repair. A stripping crew of 14 men, including the crane man, two crane chasers, and foreman, handle the day's production in eight hours. The work is done by contract. The blanks are greased by hand, a light machine oil being used. Also the sheets are trimmed and looped and the loops prepared by the contractors.

About 9 per cent of the total sheets produced are cut into strips for loops. The loops are annealed. Special machines are used for riveting the loops on the sheets. Electrically operated shearing machines are used for trimming the sheets and cutting the loops. Fig. 3 shows the size and position of the loops. At times,

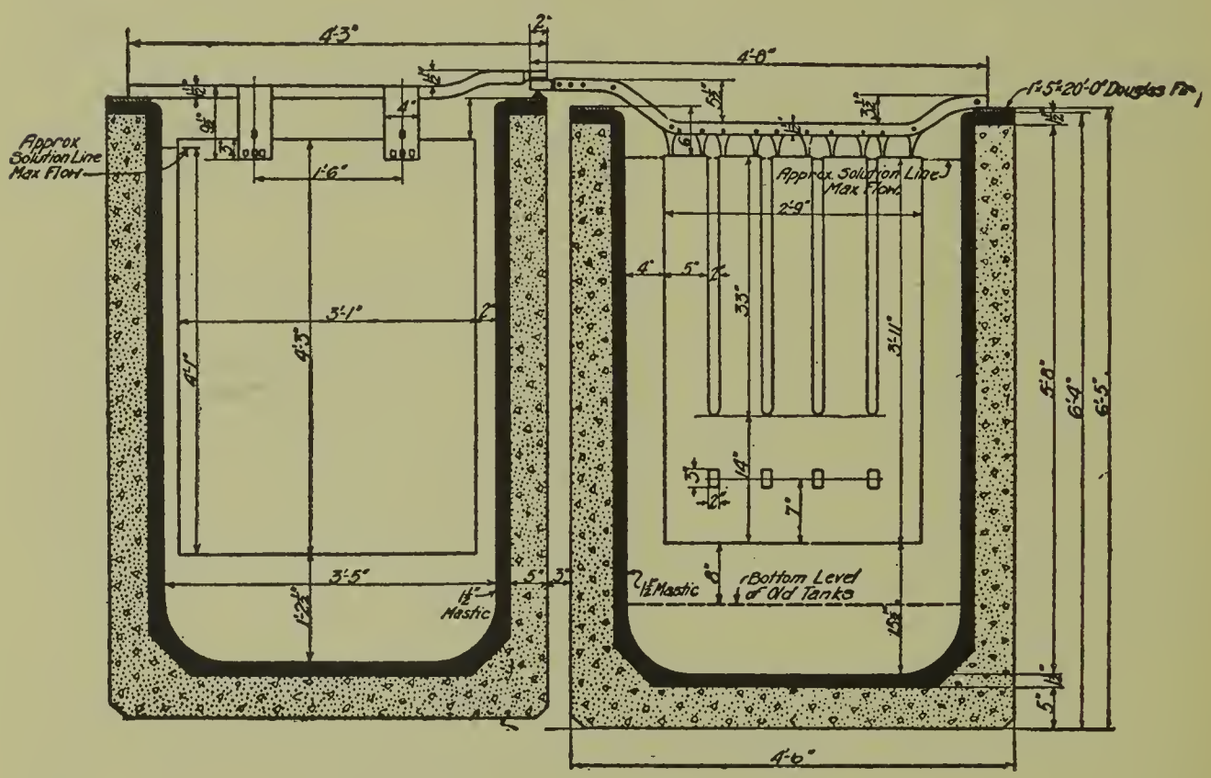

FIG. 3. Cross Section Through Tanks.

Spacing	Number Suspension Bars per Tank		Total Electrodes per Tank	No. of 5 in. (12.7 cm.) Anodes per 16-Tank Section	Cathodes c. d. Amp. per sq. ft. at 1200 Amp.
	Anodes	Cathodes			
4 in. (12.2 cm.)	56	55	111	4,480	9.05
4.5 in. (11.4 cm.)	50	49	99	4,000	10.15

considerable trouble has been experienced through failure of the loops. With the riveting machines in good order the tank house suffers little from cathodes dropping into the tanks. Extreme care is used in stripping, handling the sheets and blanks, and in revision of the anodes. An average of over 99.5 per cent serviceable sheets out of the total possible, is always obtained. The pro-

portion of starting sheet scrap averages 7 per cent of the total deposit.

Unless an entire section is going in or coming out of service, the anodes are changed as the individual case requires. The anodes are tested for weight by hand lifting. The lightest anodes and those adjacent to which poor sheets were produced, are picked up by the crane and replaced, or not, as the appearance dictates. The new anodes are hammered straight before placing in service. In this method of single replacement, no cutting out of tanks or current interruptions are necessary, so that no time is lost due to anode changing. The average anode is scrapped at about 25 per cent of its original weight.

In the original installation, antimony-lead blanks were used exclusively. Copper blanks were soon introduced, but the cost of the manufactured copper blanks and the trouble encountered due to sticking of the deposit, retarded the replacement of the lead blanks for several years. The copper blanks are unquestionably superior. At 17.8 amp./sq. ft. or 1.9 amp./sq. dm. current density, the tank voltage using copper blanks is 12 per cent lower than when using lead. Today the copper blanks are stripped more easily than the lead blanks and fewer sheets are torn in stripping. Furthermore, the sheets from the copper blanks can be straightened better, being less resilient than those produced from the lead blanks. Loops made from the former are just as tough after annealing as those made from the latter. As soon as the operators became familiar with handling the copper blanks and greater care was exercised, fewer copper blanks were stuck, and now it it rare that such a thing occurs. It was discovered that copper blanks could be made locally from the starting sheets, and thus produced, were even cheaper than the lead blanks. The lead blanks are being rapidly replaced, and now 51 of the 64 tanks in service contain copper blanks.

L. C. Fopeano, of the tank house staff, describes the manufacture of copper starting sheet blanks at Chuquicamata as follows: "The lead blanks in use in the tank house are gradually being replaced by copper blanks, manufactured by deposition in the starting sheet division. These blanks have been found equally as efficient as the imported rolled copper blanks, and can be manufactured here at a small fraction of their cost. The procedure

followed to make a copper blank is briefly given. A lead blank about 5 ft. 3 in. x 3 ft. 3 in. (160 x 99 cm.) is hung between correspondingly large soluble anodes, and a deposit of about five days formed on the blanks. The blank is stripped and the sheets cut to 4 ft. 11 in. x 3 ft. 1⅛ in. (150 x 95 cm.), the regular size of a copper blank; the holes for the crane hooks are also cut."

"The sheets are suspended from cathode bars by copper wires between the large soluble anodes in sections 1-8 for 4 or 5 days. Each day the sheets are withdrawn from the tank and scraped to remove flowers and irregularities on the surface. When the sheets are about ⅛ in. (3 mm.) thick they are hung in a special tank of sufficient depth to allow complete submergence in order to build up the sheet at the top where the bar will be riveted. This is not possible in the ordinary starting sheet tank because of its depth. In the special tank the copper is deposited from the large soluble anodes in regular starting sheet solution. The current density is low to permit a smooth, even deposit. About 5 days are necessary in this tank to build the sheet to the desired thickness, about ¼ in. (6 mm.). The sheet is scraped with steel scrapers and polished with emery cloth until perfectly smooth. A copper bar is riveted and soldered to the sheet, a coating of amalgam applied, and the blank is ready for service. Approximately 15 days are necessary to make a blank. The present capacity is two finished blanks a day."

HANDLING OF THE COPPER.

While there are no striking innovations in the method of pulling cathodes, loading starting sheets, or changing anodes, the work is accomplished efficiently and deserves mention. The house is divided into three crane bays, and in each bay there are three 10-ton Shaw cranes. The cranes are high speed, and carry 20 ft. (6 m.) racks. Such a rack will cover an entire tank. The rack hooks are so spaced that only alternate electrodes can be picked up at one time. This system of removing alternate cathodes instead of handling by half tanks, was installed to prevent the subjection of the Chilex anodes to exceedingly low densities or possible current interruptions. It should be noted that the crane serving the starting sheet sections, which is included in the nine

mentioned above, carries a ten-foot (3 m.) rack and handles adjacent blanks by half tanks.

The cranes are served entirely by hand. That is to say, no mechanical devices are employed for hanging the starting sheets on the crane rack hooks, unloading the cathodes therefrom, or releasing into or picking up sheets or cathodes out of the tank. Cathodes are pulled at an average weight of about 153 lb. or 70 kg. (140 lb. (63.6 kg.) deposition plus 13 lb. (5.9 kg.) starting sheet). A 16-tank section at 4.5 in. (10.4 cm.) spacing, produces approximately 60 short tons (54.5 m. tons) of cathode copper per run (or per pulling). At the present rate of full production an average of 6 sections per day are pulled and 6 days pulling per week. A crew of 26 men, including foremen and crane men, accomplish this work in an 8-hr. day.

The work of pulling and loading includes insertion of suspension bars in the starting sheet loops; beating the sheets straight before hanging on the crane; loading and unloading the crane; proper centering of the sheets in the tanks; washing of the cathodes; arranging the cathodes on the cars so that level piles of a standard height are formed; placing in position all material, sheets, cars, cut-out bars, etc., needed in the work; and changing anodes and cleaning tanks when necessary. From the data given in this paragraph, it can be calculated that the work is accomplished at a rate of 14 short tons (12.7 m. tons) of cathodes per man-day, supervision and crane service included. This work is done on contract, but the current efficiency does not suffer thereby. Any careless loading is penalized by forfeiture of the contract bonus.

Cathode suspension bars are cleaned at the end of each run. The method of cleaning is to steam the bars and polish the heads on a revolving wire brush. Whenever released from service, the anode suspension bars are cleaned in the same manner. During operations, the triangular bars and bus bars are cleaned at all points of contact. Once during every run, the V-ridges and grooves of the suspension bars are coated with cup grease.

INSPECTION.

Inspection service is an exceedingly important part of tank house operation at Chuquicamata. It has often been remarked

that the cathodes were unusually smooth and free from warping. This condition is not due to any inherent qualities of the anode, electrolyte, or circulation, but merely the result of extreme care and considerable labor. The straightenings, crane revisions, contact greasings, etc., are all done at definite periods during the growth of the copper. The work for every section, every shift, is performed according to schedule and written orders. This systematic attention is laid out according to results obtained through several years of study, observation, and experiment. There is casual as well as scheduled inspection, but few faults are found by the former when the latter has been systematically performed.

If the inspection service were omitted for one run, the cathodes pulled would be found badly warped and discolored. Sprouts and evidences of short circuiting would be abundant. In fact these conditions would be exhibited in an unusual degree. It has been actually demonstrated that there is no natural tendency for good copper deposition in the Chuquicamata tank house, and yet the cathodes pulled are absolutely free from the defects mentioned above or evidence of such defects having existed during their formation.

The inspectors, assistants, and sheet straighteners are all paid according to a bonus scheme, the results of which are gratifying. The cost of inspection labor is insignificant when compared with the saving effected.

SPACING.

Before 1921 the spacing of the insoluble anodes in the tank house was 5 in. (12.7 cm.) Still previous to this an attempt had been made to reduce the spacing to 4 in. (10.2 cm.) at a time when the first ferro-silicon grid anodes were introduced. The result was a decrease in current efficiency, which more than offset the gain in voltage. However, in 1921, through the encouraging results of improved inspection the attempt was renewed, and it was found that the difference in the current efficiency at 4.5 in. and 5 in. spacing was inappreciable. The insoluble anodes in the entire house were placed at 4.5 in. (11.4 cm.) spacing, and a little later, a considerable number of sections were tried on 4 in. (10.2 cm.) spacing. The current efficiency at 4 in. spacing was

not noticeably lower than at 4.5 in., and there was a considerable gain in power efficiency at the former.

At this time the Chilex anodes were being installed. As these anodes were of the 5-bar form, which is difficult of alignment, and the effects of current interruptions were greatly feared, 4.5 in. spacing was adopted as the standard for the insoluble house. The Chilex grid has now been perfected and it has been demonstrated both by calculations and actual tests, that 4-in. spacing is practical with these anodes. The gain in reduced voltage at the lower spacing will practically offset a 3 per cent decrease in current efficiency. Several sections are now being operated at 4-in. spacing, and so far it appears that without increasing the inspection service, there is no material decrease in current efficiency. Steps are being taken to install the necessary suspension bars to convert the tank house to 4 in. (10.2 cm.) "spacing."

In comparing the results at different spacings, it must be remembered that the relative capacity for depositing copper is in direct proportion to the ampere efficiency and the ampere load, and not to the current density. If the comparison be made for equal current densities, it is assumed that with the narrower spacing more load is carried, since the tanks will naturally be filled with electrodes in any case. For equal ampere loads, the narrower spacing shows lower voltage for two reasons—decreased current density and decreased ohmic resistance. In making the comparison for the same total power consumptions, the following equations were used, which equations are based on normal conditions, apply to the average Chilex anodes in service at present, and were calculated from operating data.

$$V = 1.84 + L/N\ (0.99 + 0.21\ (S-M))\ 10^{-3}$$
$$V = 1.84 + D\ (0.0239 + 0.005\ (S-M))$$
$$L = 62.5\ E/N$$
$$I = 24\ ND$$

where V= Tank voltage; D = Cathode current density in amperes per square foot; S = Spacing in inches center to center of anodes; M = Average width of 1 anode and cathode, and is taken as 1 in. (2.54 cm.) in the following calculations: I = Amp. load; N = No. of cathodes per tank; E = Percentage, current efficiency; L = Lb. copper produced per kilowatt-day.

Using the above equations, the results obtained in the tank house, for the first 15 days of September, are compared with the results that would have been obtained had the spacing been 5 in. (12.7 cm.) and 4 in. (10.2 cm.) instead of 4.5 in. (11.4 cm.). The comparisons are based upon the assumptions that the same total load (practically the maximum) was carried on the house, and that the current efficiencies would have been the same.

TABLE I.

Spacing Comparison for Equal Power Consumptions.

Spacing	5 in. (12.7 cm.)	4.5 in. (11.4 cm.)	4 in. (10.2 cm.)
Total kw. day load on house.....	27,531	27,531	27,531
Av. kw. day load per insol. anode tank	31.54	31.54	31.54
Av. current density on insol. anode tanks	12.50	11.57	10.61
Av. ampere load on insol. anode tanks	13.20	13.60	14.00
No. of cathodes per tank.....	44	49	55
Av. voltage of insoluble anode tanks	2.389	2.319	2.253
Av. current efficiency for insol. anode tanks	88.40	88.40	88.40
Av. lb. Cu per kw. day for insol. anode tanks	23.13 (10.5 kg.)	23.82 (10.83 kg.)	24.52 (11.14 kg.)
Lb. Cu per tank day for insol. anode tanks	729.5 (332 kg.)	751.30 (341 kg.)	773.40 (351 kg.)
Per cent increase or decrease in production compared to 4.5 in. (11.4 cm.) spacing	2.90 Decrease	....	2.90 Decrease
Per cent increase or decrease in power efficiency compared to 4.5 in. (11.4 cm.) spacing	2.90 Decrease	....	2.90 Increase

With ferro-silicon anodes the change of voltage per unit of density is greater than with Chilex anodes, and hence, the relative gain in capacity by decreased spacing was greater. In fact, it was about twice as great at the load considered in the above calculations. For a similar reason, with the very best Chilex anodes the gain would be a trifle less than that shown above.

It should be noted that in any case there is a gain in power efficiency, which produces the gain in production.

Tables II and III are calculated from the same equations and show the relative capacity at equal current densities and the relative capacities at equal ampere loads. These would apply if the current density or ampere load were considered the factor limiting the production. At present, the total power or sub-station equipment is practically the limiting factor, so that Table I is more applicable to present conditions than Tables II and III.

TABLE II.

Spacing Comparison for Equal Current Densities.

Spacing	5 in. (12.7 cm.)	4.5 in. (11.4 cm.)	4 in. (10.2 cm.)
Total kw. day load house.....	27,531	27,531	27,531
Av. kw. day load per insol. anode tank	28.69	31.54	34.97
Av. current density on insol. anode tanks	11.57	11.57	11.57
Av. ampere load for insol. anode tanks	12.22	13.60	15.27
No. of cathodes per tank	44	49	55
Av. voltage of insol. anode tanks.	2.348	2.319	2.29
Av. current efficiency of insol. anode tanks	88.40	88.40	88.40
Av. lb. Cu per kw. day insol. anode tanks	23.53 (10.7 kg.)	23.52 (10.69 kg.)	24.13 (10.96 kg.)
Av. lb. Cu per tank day insol. anode tanks	675 (304 kg.)	751 (341 kg.)	844 (384 kg.)
Per cent increase or decrease in capacity compared to 4.5 in. (11.4 cm.) spacing	10.10 Decrease	....	12.40 Increase
Per cent increase or decrease in power efficiency	1.20 Decrease	....	1.30 Increase

Table II indicates what the possibilities are for increasing the capacity of the house without the construction of additional tanks, should the sub-station equipment be augmented. An increased power efficiency accompanying the increased capacity is indicated, when the limiting factor is considered to be the current density.

If the limiting factor were the circuit voltage, and the gain in power efficiency be sacrificed for capacity, it can be readily deduced from this table, that the capacity increase by decreased spacing would be even greater.

Table III indicates the possibilities of increasing the power efficiency by decreasing the spacing, where the production is the

TABLE III.

Spacing Comparisons for Equal Ampere Loads.

Spacing	5 in. (12.7 cm.)	4.5 in. (11.4 cm.)	4 in. (10.2 cm.)
Total kw. day load on house.....	27,531	27,531	27,531
Av. kw. day load per insol. anode tank	32.71	31.54	30.48
Av. current density on insol. anode tanks	12.88	11.57	10.30
Av. ampere load on insol. anode tanks	13.60	13.60	13.60
No. of cathodes per tank.....	44	49	55
Av. voltage of insol. anode tanks.	2.405	2.319	2.241
Av. current efficiency anode tanks.	88.40	88.40	88.40
Av. lb. Cu per kw. day insol. anode tanks	22.97 (10.44 kg.)	23.82 (10.83 kg.)	24.65 (11.10 kg.)
Av. lb. Cu per tank day insol. anode tanks	751 (341 kg.)	751 (341 kg.)	751 (341 kg.)
Per cent increase or decrease in power efficiency compared to 4.5 in. (11.4 cm.) spacing	3.60 Decrease	....	3.50 Increase

limiting factor, assuming that the amount of power developed can be regulated efficiently to meet the requirements of production.

As stated before, Table I simply applies to a condition where the amount of available power is the limiting feature. In this case, the increase in capacity is exactly that due to the increase in power efficiency. This means production increase with a decreased power cost per unit of copper produced, but no decrease in total power cost.

The preceding tables and deductions assume no decrease of current efficiency. Therefore, no definite conclusions should be

based thereon until further data are obtained from the sections operating at 4 in. (10.2 cm.) spacing. However, there is no indication to date that would permit of the assumption that the current efficiency will be decreased by a reduction of the spacing from 4.5 in. (11.4 cm.) to 4 in. (10.2 cm.). The reduction from 5 in. (12.7 cm.) to 4.5 in. (11.4 cm.) resulted in an indisputable gain of power efficiency, and in this case there was no apparent loss of current efficiency

ELECTRICAL EQUIPMENT, LEADS, ETC.

Alternating current transmitted from the power station at Tocopilla, is converted to direct current in the main sub-station at Chuquicamata, and thence transmitted to the tank house. The sub-station installation for this service consists of the following equipment:

Three synchronous motor-generator sets, with maximum capacity of 2500 kw., d. c., and maximum generator amperage of 10,600 at 265 v.

Four asynchronous motor-generator sets, same capacity as above.

Four rotary converters, with maximum capacity of 3480 kw., d. c., and maximum generator amperage 12,000 at 290 v.

Two motor-generator sets, with maximum capacity of 900 kw., d. c., and maximum generator amperage of 3750 at 240 v.

The power is transmitted from the sub-station to the sections and between sections in the tank house, by leads consisting of 5 laminations of cold-rolled copper plate. The plates are 9 x ½ in. (22.8 x 1.3 cm.). At the end of each section 2.5 x 10 in. (6.4 x 25.4 cm.) bus bars are used. These are of cold-rolled or locally cast copper. The conductivity of the latter is only 3 per cent less than the former which are imported, so that without doubt, all bus bars installed in the future will be cast in the Chuquicamata smelter. All joints in the leads, and between leads and bus bars, are amalgamated, the amalgam used for this purpose consisting of 5 parts of mercury, 3 of tin and 1 of silver.

The total length of leads between the machines in the sub-station and the sections in the tank house is 4289 ft. (1308 m.). The lead loss is approximately 2 per cent of the gross d. c. power delivered by the machines, while the power lost in stray currents

and in grounds is about 1 per cent. The net available power, bus bar to bus bar of the sections, can, therefore, be figured as about 97 per cent of the total d. c. power developed by the machines. This d. c. power in turn is about 92 per cent of the a. c. power converted for this purpose.

Between tanks, triangular bars of 25/32 sq. in. (5.04 sq. cm.) cross-section area and running the full length of the tank, serve to distribute the current between the electrodes. The V-notch grooves in the heads of suspension bars form an angle of 58°, the V-ridges thereon and the sides of the triangular bars, forming angles of 60°.

TANK LININGS.

Since the great success of the leaching process as carried on in Chuquicamata may be, in a measure, attributed to the development of the acid-proof mastic lining for concrete, and since the same mastic lining solved the problem of the lead corrosion in the tank house, due to the relatively high nitric acid content, a few remarks about this particular phase of the work may not be amiss.

The department, at present, consists of about 180 men whose duty it is to keep in repair 9 leaching vats, 10 solution sumps, 25 settlers in the dechloridizing plant and 894 electrolytic tanks in the tank house, besides about 2 mi. (3.2 km.) of mastic pipe which are still in use. A close estimate of the mastic in use in Chuquicamata today places the total area at 905,000 sq. ft. (84,200 sq. m.).

Since the introduction of mastic here about 9 years ago, the essential changes, besides various alterations in the formula of the mixes, have been:

1. The gradual replacement of all mastic pipe lines by wood stave lines.
2. The gradual replacement of all concrete mastic-lined launders by solid reinforced mastic launders.
3. The superseding of a thin-walled lining containing only expanded metal by a heavily armored, thick wall for all solution sumps and leaching vats.

The new type of lining for the leaching vats consists, in reality, of a huge mastic box placed within a concrete shell. This idea,

combined with the solid mastic launders, forecasts one more step, that is, all mastic electrolytic tanks, or even the possibility of one large tank with partitions to take the place of the 16 individual tanks which now constitute a section. Incidentally, several reinforced mastic tanks, some as much as 12 ft. long x 5 ft. deep (3.66 x 1.53 m.) are already in use in the dechloridizing plant.

COPPER.

The marketable copper is of an average purity of 99.96 per cent copper. Its conductivity, on the Mathiessen standard, is 98.7 for the hard copper and 100.9 for the annealed.

DISCUSSION.

E. L. JORGENSEN[3]: The new anode invented and worked out by Dr. Colin G. Fink and his staff in the research laboratory of the Chile Exploration Company's metallurgical department, of which E. A. Cappelen Smith is the head, has in practice reduced the cell-voltage about one-third and increased the ampere efficiency because it introduces no iron. Had the iron already present in the electrolyte not decreased, the ampere efficiency with the new copper silicide anode would have been lower than with the ferrosilicon anode formerly used, because an anode with low voltage oxidizes ferrous iron much more readily than an anode with high voltage. I believe this holds good and, in general, offers food for thought and research.

The saving in power resulting from the introduction of the new anode made the existing power plant able to take care of increased tank house production, saving several million dollars. The cost of anode maintenance was reduced by about 90 per cent, saving in addition about $1,000,000 per year. This is a brilliant example that foresight in research often pays handsomely. In the laboratory certain lots of synthetic electrolyte made to correspond closely to the electrolyte used at the plant gave with the same anodes widely different voltages and changes in voltages after current interruptions. When these results came

[3] Irvington Smelting and Refining Co., Irvington, N. J. Formerly with Chile Exploration Co., Chuquicamata.

to my notice, I conducted an investigation which showed that small changes in chlorine content of the electrolyte, from say 0.5 to 0.6 grams per liter, would cause distinct voltage fluctuations and that a small amount of manganese had a great influence. To introduce iron into the synthetic solutions, commercial iron sulfate was used, which was found to contain considerable amounts of manganese. This, of course, had great bearing on the practical operations showing the importance of controlling these impurities. Fortunately, the reduction of iron and the reduction in voltage by the new Chilex anode went hand in hand, and that result was a great reduction in power, in both lowering the voltage and in improving the ampere efficiency besides reducing the anode cost itself.

CHAS. H. ELDRIDGE[4] This description of the tank house practice at Chuquicamata is an important contribution to the literature of copper hydrometallurgy. I should like to refer briefly to some of the many early troubles experienced with insoluble anodes before the adoption of the Chilex anode in 1921.

At first a magnetite anode of German manufacture was tried out with little or no success. Next a Duriron anode was tried out, and for a number of years a cast ferrosilicon anode of essentially the same composition as Duriron (13-15 per cent Si) was used at the plant. As an anode, ferrosilicon worked satisfactorily except that as it corroded away at the rate of 5-10 lb. per 100 lb. of copper deposited, it continually introduced iron into the electrolyte, with consequent lowering of the current efficiency. This necessitated a continual bleeding or discarding of spent electrolyte in order to hold down the iron content. An elaborate cooling system was also required in order to keep the electrolyte below 30° C., because of the high iron in solution.

It is most interesting that primarily in consequence of the introduction of the insoluble Chilex anode, it has been possible to shut down the sulfuric acid plant and to dispose with the cooling towers. The new anode has reduced the total iron from 20 down to 4 g. per liter.

The "Chilex" anode is the direct outcome of the four years of patient research at the New York Laboratories of the Chile

[4] Research Metallurgist, Metropolitan Museum of Art, New York City. Formerly Metallurgist, Chile Exploration Co. Laboratories.

Exploration Co. This work was under the immediate direction and continual encouragement of Dr. Colin G. Fink, the inventor of the "Chilex" anode.[5] Sometimes as many as ten men were giving full time to the problem, and, as my metallographic and corrosion tests will show, there were fully 3000 anodes, representing about 25 binary and ternary types of alloys, that were painstakingly tried out and correlated.

The Chilex anode is essentially a complex cuprosilicon alloy, with about 70 per cent Cu. Only by adding small percentages of Mn were we able to cut the corrosion to less than 1 lb. per 100 lb. of Cu deposited. The small amount of lead present serves to reduce anode voltages from 4 volts or over to the values of 2.3 to 2.5 as given.

Many other interesting anodes were developed, but the Chilex was selected because it was low in iron, insoluble, of a voltage lower than that of ferro-silicon, and had the nearest to "100 per cent copper composition."

COLIN G. FINK[6]: I appreciate the complimentary remarks of Mr. Jorgensen and Mr. Eldridge, and I would like to take this occasion to say that in the development of this copper silicide anode there were quite a number who co-operated with me and whose co-operation I appreciated very much indeed. The anode was christened "Chilex" by Mr. Eldridge. In the development of the anode alloy we were often asked: "How can you select a metal like copper and make copper insoluble when copper is the very metal which is readily soluble in the electrolyte?"

When it comes to producing electrolytic copper, we must live up to stringent specifications laid down by the big electrical manufacturers, who insist on a certain high purity and high electrical conductivity. Now if you start out with an alloy anode that contains metal ingredients which will go into solution and be co-deposited with the copper, the electrical conductivity will promptly drop. Strictly speaking, the only metal that is permissible in a copper solution is copper. So the only thing to do is to make an anode of insoluble copper. The ideal insoluble anode for copper electrolysis is composed of nothing but copper (to obtain maximum electrical conductivity in the anode) and a thin

[5] U. S. Patents 1,441,567 and 1,441,568.

[6] Head, Division of Electrochemistry, Columbia Univ., New York City.

surface film that will catalyze the formation of oxygen in preference to the formation of copper sulfate.[7]

A. W. ALLEN[8] (*Communicated*): We ought not to use the word "tank" when referring to the apparatus in which electrolysis occurs. The frequent repetition of "tank" in the opening paragraphs is followed by the use of the same word to refer to vessels for the storage of treated and untreated solution. That confusion results is evidenced by the fact that it is necessary to explain that the "outflow from the tanks" is spent electrolyte.

The system of nomenclature criticized has, it must be admitted, received wide approval; but it is suggested that its continued use indicates adherence to a custom established without apparent regard to scientific accuracy or a desire for clarity in descriptive presentation. The electrochemistry of copper is a comparatively recent science, and it is to be hoped that future generations will not be burdened with illogical precedent that leads to confusion, if not unintelligibility. A tank is used for the storage of liquids; a suitable word to refer to a vessel containing electrodes and an electrolyte is "cell." The speaker has had the temerity to mark this distinction in published matter; and it would be interesting and informative to know the reasons for the retention and the extended use of the present system of nomenclature. If there is justification for what appears to be accepted usage among operators, a definition of "tank," as used in the hydrometallurgy of copper, would clarify the literature of the subject and help to prevent the confusion that results if the word is also used in its commonly recognized sense. From contemporary technical literature, it is difficult to understand whether it refers to the mastic-lined cement vessel, or to the complete apparatus.

The results now being obtained by the use of the new anode are reflected in lower cost per pound of copper produced, which averaged 8.1 cents per pound in 1923, as compared with 18.55 cents per pound in 1915 and 15.46 cents per pound in 1916.

Statistics of tonnage treated and extraction obtained at Chuquicamata indicate the benefits accruing from metallurgical and

[7] See in this connection discussion at the Cambridge Symposium on Catalysis, Jan., 1924. Ind. and Eng. Chem., 16, 566.

[8] Assistant Editor, Chemical and Metallurgical Engineering, Engineering and Mining Journal, San Francisco, Calif. The above discussion was presented at the meeting of the California section, American Electrochemical Society, May 27, 1924.

electrochemical research. In 1915 the plant treated 625,394 tons, the extraction of copper being 66.87 per cent. In 1916, 1,742,748 tons were treated, the extraction being 77.15 per cent. It was not until about 18,000,000 tons had been treated, and experience extending over five years or so had been gained, that an average yearly extraction of 90 per cent was reached. And it was not until after about 22,000,000 tons had been treated and various anodes tried out that the Chilex anode was developed and adopted. The net result of operations at Chuquicamata indicates the importance of adequate capital, unhampered research and moral support in any new enterprise of this kind. The technical history of the Chile Exploration Co. shows how great a mistake would have been made if the venture as a whole had been condemned, and research deflected into another channel, on account of the low metallurgical extraction and comparatively high cost of production during the initial stage of operation.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, Mr. S. Skowronski in the Chair.

ADDITION AGENTS IN TIN REFINING ELECTROLYTES.[1]

By Edward F. Kern[2] and Edward A. Capillon.[2]

Abstract.

The effect of various addition agents on the cathode deposit of tin was investigated. The major portion of the tests was confined to acid tin sulfate and acid tin-sodium sulfate electrolytes. Chloride electrolytes were tried, but results were unsatisfactory. The addition of 5 g. HCl (or 9 g. NaCl) per L. of electrolyte improved the quality of the cathode deposit, and furthered the uniform corrosion of the anode. Of the addition agents tried, glue was found to give the best results. Even when other addition agents were employed, the presence of glue seemed to be essential to insure uniform smooth, bright, adherent cathode deposits of tin. The quantity of any addition agent added must be kept within well-defined limits; an excess causes non-adherent amorphous-like deposits of tin; if too small a quantity of an addition agent is present the deposits are coarsely crystalline. Cathode deposits from sulfate electrolytes kept at 47° C. were not as adherent nor otherwise as satisfactory as cathode deposits from the same electrolytes kept at 23° C. [C. G. F.]

It is essential in the electrolytic refining of metals to produce dense, smooth, and adherent cathode deposits. Tin is one of the metals which, during electrolysis, tends to be deposited in the form of non-adherent crystals, which soon short-circuit the electrodes. In order to obtain a desirable cathode deposit it is not only essential to use a tin electrolyte which is not readily hydro-

[1] Manuscript received February 15, 1924.

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lyzed, but we must make the proper additions of colloid materials which will cause the tin to be electrolytically deposited in compact form.

An abstract of the literature on the electrodeposition and electrolytic refining of tin has been published.[3] Conditions which are necessary for the electrolytic refining of tin and for the formation of dense, smooth, and adherent cathode deposits are as follows:

a. The electrolyte should be a tin salt which is very soluble, and which is not readily hydrolyzed.

b. The tin content of the electrolyte should have a definite relation to the current density at which the refining is conducted; the higher the current density used the higher must be the tin content.

c. The electrolyte must be pure with respect to metals which stand below tin in the e. m. f. series.

d. Presence of suitable colloid addition agents is essential in order to prevent the deposition of tin as non-adherent crystals; the use of the proper addition agent causes the tin to deposit on the cathode in a smooth, dense, pure, and adherent form.

e. The circulation of the electrolyte must be at such a rate that segregation of the constituents and polarization do not occur.

f. There must be present a suitable salt or acid which will form an insoluble precipitate with lead, a common impurity in tin anodes, as lead and tin have practically the same position in the e. m. f. series.

g. The electrolyte must be heated, as the potential drop is thereby lowered. Provided the temperature does not exceed about 40° C., the anodes are more evenly corroded in a warm electrolyte, and as a rule the smoothness and adherency of the cathode deposit is better.

The electrolytes which have proven most satisfactory for electrolytically refining tin are the fluosilicate, fluoborate, sulfate, mixture of sulfate with either fluosilicate or fluoborate, and the double salts of tin-sodium and tin-ammonium chlorides. Satisfactory cathode deposits have also been produced in tin per-

[3] Trans. Am. Electrochem. Soc., 23, 193-232 (1913); 33, 155-168 (1918); 38, 143-166 (1920).

chlorate electrolytes. In each case, addition agents are required in order to produce dense adherent deposits. An abstract of the literature on "Addition Agents in Tin Electrolytes" has been published.[4]

ROLE OF ADDITION AGENTS.

A paper entitled "Role of Colloids in Electrolytic Metal Deposition" has recently been published by H. J. S. Sands.[5] The article is a review of the literature relating to addition agents. It also gives the "theories as to the cause of effect of addition agents in electrolytes." The statement is made that "no general rules are known by means of which the effect of adding any particular agent to a given solution may be predicted." "The addition agent is precipitated along with the deposited metal, so periodic additions must be made."[6] "It is essential that the addition agent added to the electrolyte should travel to the cathode, where in virtue of its viscid nature it acts as a diaphragm, checking circulation of the electrolyte and hindering the growth of metal crystals, particularly where there is a strong tendency for crystal growth."[7]

"Addition agents which, as a rule, exert the most favorable effect upon the electrodeposited metal are those which form disperse system with the electrolyte." "The very great dispersion of nuclei produced when colloids are present has a great influence upon the subsequent structure of the electrodeposit, causing with small quantities of colloid the micro-crystalline form. The effect of large amounts of colloids is to produce amorphous layers of the deposited metal intermixed with the colloid."[8] "The rate of crystalline growth in liquids is greatly diminished by presence of colloids, which are adsorbed by the crystal surfaces. Most addition agents are adsorbed by the solid metals, independent of the current. The amount of free acid, or of free alkaline, in an electrolyte, affects the influence of the addition agent.[6]

Theories of electrodeposition of metals and the function of

[4] Trans. Am. Electrochem. Soc., 38, 145-149 (1920).

[5] "Fourth Report on Colloid Chemistry by the British Association for Advancement of Science," pp. 346-356 (1922).

[6] *Loc. cit.*, p. 347.

[7] *Loc. cit.*, p. 352.

[8] *Loc. cit.*, p. 353.

[9] *Loc. cit.*, p. 348.

addition agents have been advanced from time to time. Snee's theory was presented by Bancroft,[10] and the "reducing colloid film" theory by Kern.[11]

A study of a compilation of effective addition agents suggests that the desirable active addition agents are those materials which, when added to the electrolyte, form a dilute emulsion, or a disperse system with the electrolyte, and which exist as colloids in the solution. The addition agents which were used for conducting the experimental part of this research were selected with these ideas in mind.

TABLE I.

Composition of Tin Electrolytes.

No.	Grams per Liter				Remarks
	Tin	Free H_2SO_4	SO_4 (Metal)	Free HCl	
1, a	60	75	...	..	$SnSO_4$ solution
1, b	60	100	...	..	$SnSO_4$ solution
1, c	60	135	...	..	$SnSO_4$ solution
2	60	100	72. g. Na_2SO_4	..	$SnSO_4.Na_2SO_4$ solution, corresponding to double salt
3	60	100	61. g. $MgSO_4$	..	$SnSO_4.MgSO_4$ solution, corresponding to double salt
4, a	60	...	...	10.	$SnCl_2$ solution
4, b	60	...	...	20.	$SnCl_2$ solution
5, a	60	...	...	10.	$SnCl_2.2NaCl$ solution, corresponding to double salt
5, b	60	...	...	20.	$SnCl_2.2NaCl$ solution, corresponding to double salt
6, a	60	...	...	10.	$SnCl_2.MgCl_2$ solution, corresponding to double salt
6, b	60	...	...	20.	$SnCl_2.MgCl_2$ solution, corresponding to double salt

EXPERIMENTAL PART.[12]

Eleven electrolytes were selected for the tests; they contained 60 g. per L. of stannous tin, or approximately normal solutions. The compositions are shown in Table I.

[10] Trans. Am. Electrochem. Soc., **21**, 239-243 (1912).
[11] Trans. Am. Electrochem. Soc., **15**, 472 (1909).
[12] The experimental part was conducted by Edward A. Capillon in the non-ferrous laboratory of the School of Mines of Columbia University, in partial fulfillment of the requirements for the degree of Metallurgical Engineer in 1923.

PREPARATION OF THE ELECTROLYTES.

The five sulfate solutions (1, a; 1, b; 1, c; 2, and 3) were made by preparing a definite copper sulfate solution containing the required amount of free sulfuric acid, and replacing the copper by means of granulated tin in a cell arranged similar to an ordinary Daniell "gravity" cell. Solution 2 contained the required amount of sodium sulfate; and solution 3 contained magnesium sulfate, each in equivalent amounts to form their respective double salts with the tin sulfate. Complete replacement of the copper by the tin took place readily. Free H_2SO_4, to prevent the tin salt from hydrolyzing, was present in less than the approximate amounts to give a solution containing either 75, 100, or 135 g. per L.

After complete replacement of the copper by the tin had taken place, the solutions were analyzed for tin and total sulfuric acid content, and if necessary the free sulfuric acid content adjusted by making the required addition. The scheme of replacing the copper electrochemically by the Daniell "gravity" cell arrangement was found satisfactory, whereas the direct replacement by placing granulated tin in acidified copper sulfate solution was extremely slow and not complete, as in the latter case the granules of tin immediately became coated with a dense deposit of copper which retarded the replacement.

The procedure for making the tin sulfate electrolytes was to place the copper sulfate solution in a large beaker; introduce a copper electrode, which occupied the upper section of the beaker; from the copper electrode to the bottom of the cell an electric circuit was established by means of a copper wire, which was insulated from the solution by a glass tube, except at the bottom of the cell, where the copper wire was curled into a flat spiral. On top of the copper spiral were placed small pieces of pure tin. The copper was electrolytically deposited upon the copper electrode, and the tin went into solution, the color of the solution in the cell changing from blue to colorless. The end of the replacement was indicated by a complete decolorization of the solution, and the appearance of the copper deposit on the electrode, which, at the end of replacement, formed as non-adherent

black amorphous precipitate. Heating the cell to between 50 and 60° C. hastened the replacement.

The six chloride solutions (4, 5 and 6) were made by dissolving weighed amounts of the chlorides in water, which contained the free hydrochloric acid, and diluting to volume.

PREPARATION OF THE ADDITION AGENTS.

The addition agents we tested are the following: Glue; Oil Emulsion; "Sol Cut" Oil Emulsion; Cresol; "Creolin-Pearson" Emulsion; Cresol Sulfonate; Nicotine Sulfate; and Aloin. These were used alone and as mixtures.

Glue Solution: The variety of glue used was "dry bone" glue, which was previously found to be a much better addition agent than either "green bone" or "hide" glues. A weighed amount of the glue was soaked in a small amount of cold water for about half hour, then it was readily soluble in hot water. The solution must not be boiled, as boiling brings about certain changes in the glue, which destroy its valuable property as an addition agent. The glue solution should be prepared as needed, as it tends to deteriorate on standing.

Oil Emulsion: The usual way of emulsifying oil is by blowing steam through it first, to form myriads of small globules which easily emulsify with large quantities of water; the time required is long, and the amount of water which condenses with the oil becomes excessive, especially for laboratory operations. It was found that rapid emulsification of the oil could be accomplished in two ways. One gram of light fuel oil was mixed with 5 cc. of ethyl alcohol and added to enough water to make 50 cc. of emulsion, which after shaking was added immediately to the electrolytes; on standing, the oil slowly separated from the emulsion. It was also found that petroleum oil can be emulsified by the addition of a soluble colloid; for instance, when 2 g. of fuel oil was stirred into 50 cc. of water solution containing 5 g. of glue, the oil was completely emulsified. So when both glue and oil were to be added to an electrolyte, this method of preparing the emulsion was used and a measured portion added.

"Sol Cut" Oil Emulsion: "Sol Cut" oil is the trade name of a preparation used for lubricating wire dies, reamers, saws, etc.

It gives a permanent emulsion with more than eight volumes of water; it is probably a mixture of lubricating oil and rosin soap or similar organic material.

Cresol: Cresol is soluble in water to the extent of 1 part in 200 water; its formula is $C_6H_4.CH_3.OH$, and it occurs in three modifications (ortho-, meta-, and para-); crude cresol is a mixture of the three in varying proportions. The solution used in the tests was prepared by dissolving 4 g. of the crude cresol (U. S. P.) in 1 L. of water and the desired portion added.

"Creolin-Pearson" Emulsion: Creolin-Pearson is a well-known household disinfectant, which is prepared by adding cresol or a similar coal tar derivative to a strong solution of rosin soap or strong alkali soap. It gives a milky-white emulsion when added to water.

Cresol Sulfonate: This is prepared by adding cresol to a molecular equivalent of cold concentrated sulfuric acid. The temperature must not rise above 100° C. The reaction mixture is then heated to 100° and kept there for about an hour. Cresol sulfonate, $C_6H_3.CH_3.OH.SO_3H$, is very soluble in water. Tin cresol-sulfonate is likewise very soluble in water.

Nicotine Sulfate: This preparation is sold in concentrated form as an insecticide, usually containing 40 per cent nicotine. Its formula is given as $C_{10}H_{14}N_2.H_2SO_4$; it is very soluble in water.

Aloin: Aloin is a derivative of anthracene ($C_{14}H_{10}$), which is obtained from the aloe plant; its formula is generally given as $C_{17}H_{18}O_7$, but its exact constitution is unknown. The purified material is dark yellow and finely crystalline, whereas the crude material is a dark-brown resinous mass; the latter is the more effective addition agent. Curacao aloes was used; it is readily soluble in more than four parts by weight of hot water, but slowly soluble in cold water. The solution was prepared, with hot water, as needed.

PREPARATION OF THE ANODES AND CATHODES.

The anodes were made to contain 94 per cent tin, 4 per cent lead, 1.5 per cent copper, and 0.5 per cent antimony; and cast as plates 2 in. wide, 0.5 in. thick, and 3.25 in. long (5.1 x 1.3 x 8.25

cm.). The anodes were immersed 2.8 in. (7.1 cm.) in the electrolyte.

The cathodes were strips of sheet tin, prepared by rapidly pouring molten tin over an inclined iron plate (about 30°) from an oblong trough ladle held horizontally at the back of the upper edge of the inclined iron plate, the tin solidifying as a thin sheet. Cathodes 2 in. wide and 3.25 in. long (5.1 x 8.25 cm.) were cut from the sheets, and immersed 2.8 in. (7.1 cm.) in the electrolyte.

ARRANGEMENT OF THE CELLS AND OPERATION.

The cells were 400 cc. Pyrex beakers, which contained 300 cc. of electrolyte. The electrodes were suspended from two glass rods, which rested on the top of the beaker; the distance between the faces of the electrodes was 2 in. (5.1 cm.). A series of similar tests were run at the same time by connecting the cells in series, thus passing the same amount of current through each cell. The temperature of the electrolytes was maintained constant by placing the cells in a water-bath, kept at constant temperature (0.5° C.) by means of a toluol thermostat regulator.

The first series of tests were made in order to determine the effect of the variation of free sulfuric acid upon the character of the cathode deposit (see Table II). There was no apparent difference in the size of the crystals which formed, nor in the adherency of the deposit to the cathode, in the electrolytes which contained 75 and 100 g. free H_2SO_4 per L.; but in the electrolytes containing 135 g. free H_2SO_4 per L., the deposits were composed of a mass of larger crystals which were loosely attached to the cathode. It was also noticed that the amount of free acid in the sulfate electrolytes had a decided effect upon the hydrolysis of the tin sulfate.

Accordingly, five solutions were prepared to contain respectively 75, 100, 135, 150 and 200 g. free sulfuric acid, and 60 g. tin, as $SnSO_4$, per L. These five solutions were placed in stoppered bottles and allowed to remain undisturbed for three weeks, when the first inspection was made. It was found that the least hydrolysis had occurred in the solution which contained 100 g. free sulfuric acid per L.; considerable hydrolysis had taken place in the solutions containing 75 g. and 135 g. free acid; more in the solution containing 150 g. free acid; and most in the one which

contained 200 g. free acid per L. The tin content was not determined at the time, but the solutions were allowed to remain undisturbed for eight months. All of the solutions, at the end of this period, contained precipitates, but the colors of the solutions varied.

The solutions containing 75 and 100 g. free acid per L. were colorless and clear, those containing 135 and 150 g. free acid per L. were yellow and turbid, and the one containing 200 g. free acid per L. was yellow and clear. All the solutions were filtered, and their soluble tin content determined by titration with 10/*N* iodine solution; the determinations being made on duplicate portions, both before and after reduction with metallic nickel in presence of hydrochloric acid. The results are tabulated for comparison.

Solution containing Free H_2SO_4 g./L.	Soluble Tin Content by Titration:	
	Before Reduction g./L.	After Reduction g./L.
75	52.6	53.3
100	51.3	52.9
135	51.6	56.4
150	52.7	56.2
200	51.5	54.9

The results of the titrations show that the solubility of stannous sulfate in 1 L. of solution containing from 75 to 200 g. free sulfuric acid is approximately 95 g., equivalent to approximately 52 g. tin. The titrations also show that stannous sulfate in sulfuric acid solution is not readily oxidized, and is a stable electrolyte for refining of tin, if the tin does not exceed approximately 60 g. and the free sulfuric acid is between 75 and 200 g. per L.

The next series of tests were with sulfate electrolytes (2 and 3), which contained 100 g. of free sulfuric acid, 60 g. of tin as stannous sulfate, and an equivalent of sodium sulfate and of magnesium sulfate to form the respective theoretical double salts. That is, one solution contained an equivalent of Na_2SO_4 to form $SnSO_4.Na_2SO_4$; and the other solution contained an equivalent of $MgSO_4$ to form $SnSO_4.MgSO_4$. The presence of the $MgSO_4$,

without and with addition agents, was found to be detrimental, in that it not only decreased the conductivity of the solution, but also caused the tin to form a more voluminous mass of non-adherent crystals. The presence of Na_2SO_4, however, was beneficial, as it caused better deposition and had about the same effect upon depressing the conductivity of the solution. The deposits formed in the stannous-sodium sulfate solutions were more dense and more adherent than those formed in the corresponding stannous sulfate solutions (1, b) which did not contain sodium sulfate.[13]

The effect of the presence of a small amount of hydrochloric acid in the sulfate electrolytes was next determined, as previous tests, which were made with lead anodes in sulfate electrolytes, showed that the presence of a small amount of chloride caused the lead anodes to disintegrate more rapidly, and also caused the film of lead peroxide to peel from the anode. One of the difficulties experienced in the refining of tin anodes which contain lead is the formation of a coating of dense, adherent, lead peroxide. Accordingly it was thought that the addition of hydrochloric acid would likewise be beneficial for tin anodes.

The amount of hydrochloric acid which was found to be most beneficial was in the proportion of 5 g. (or 11 cc. of conc. hydrochloric acid, sp. gr. 1.192) per L. electrolyte. The effect of the presence of this amount of hydrochloric acid was to reduce the potential drop, and to cause the anode residues to become non-adherent; if a larger amount than approximately 10 g. of HCl per L. of electrolyte was added, it caused the cathode deposit to assume a more crystalline formation and to become less adherent. It was also found that sodium chloride can be used instead of the hydrochloric acid, the amount added being in the proportion of approximately 8 g. per L. of electrolyte.

Table II shows the effect of the composition of tin sulfate electrolytes upon the potential drop and the character of the cathode deposits.

EFFECT OF ADDITION AGENTS.

Eight series of preliminary runs were made in order to determine which of the ten sulfate electrolytes would be the most

[13] Compare Fink, Mining and Metallurgy, 4, 573 (1923).

TABLE II.

Effect of Composition of Tin Sulfate Electrolyte upon Potential Drop.

Current density = 15 amp. per sq. ft. (1.7 amp. per sq. dm.) Distance between electrodes = 2 in. (5.1 cm.) Temperature of electrolytes = approximately 23° C. Time of test, 90 min.

No.	Composition of Electrolytes, g. per L.				Potential Drop between Electrodes		Remarks
	Tin	SO_4 (Metal)	Free H_2SO_4	HCl	At Start v.	90 min. after v.	
1, a	60	..	75	..	0.21	0.19	(1)
A	60	..	75	5	0.20	0.16	(2)
1, b	60	..	100	..	0.18	0.12	(3)
B	60	..	100	5	0.14	0.14	(4)
1, c	60	..	135	..	0.14	0.13	(5)
C	60	..	135	5	0.12	0.11	(6)
2	60	72. g. Na_2SO_4	100	..	0.18	0.19	(7)
D	60	72. g. Na_2SO_4	100	5	0.19	0.19	(8)
3	60	61 g. $MgSO_4$	100	..	0.21	0.18	(9)
E	60	61 g. $MgSO_4$	100	5	0.19	0.17	(10)

1. Mass of non-adherent needles, some dendrites on edge of cathode.
2. Mass of non-adherent, very fine needles.
3. Mass of needles on surface; spears and arborescent dendrites on edges of cathode.
4. Mass of very fine, long needle crystals over entire surface of cathode. Non-adherent.
5. Similar to 1, a. Coarser.
6. Mass of very fine needles over entire surface of cathode.
7. Mass of needles over surface and coarse dendrites on edges of cathode. Non-adherent.
8. Mass of compact, fine needles over surface of cathode. Non-adherent.
9. Mass of very coarse, non-adherent spears and needles over surface of cathode.
10. Mass of fine needles and large spears over surface, and large dendrites on edges of cathode. Non-adherent.

satisfactory ones for refining of tin, and to enable the selection of the most promising of the eight addition agents and mixtures of same which would produce solid adherent deposits of tin. The electrolytes which gave promise of being the most satisfactory were the stannous sulfate and the sodium-stannous sulfate solu-

tions which contained 100 g. free sulfuric acid and 5 g. hydrochloric acid per L. The proportion of the addition agents which was found to give the best results when used alone is as follows:

Glue: 1 g. per L. of electrolyte.
Light Fuel Oil: 0.5 g. per L. of electrolyte.
"Sol Cut" Oil: 0.5 g. per L. of electrolyte. Similar to light fuel oil.
Cresol: 0.5 to 1 g. per L. of electrolyte.
"Creolin-Pearson": 1 g. per L. of electrolyte. Similar to cresol.
Cresol Sulfonate: 5 to 20 g. per L. of electrolyte.
Nicotine Sulfate: 1 to 2 g. per L. of electrolyte.
Aloin: 2 to 4 g. per L. of electrolyte.

The addition agents were added as water solutions, or as emulsions, which were prepared as given above under "Preparation of Addition Agents." "Sol Cut" oil acted similar to the light fuel oil, and "Creolin-Pearson" similar to cresol; so for the subsequent tests, the light fuel oil and cresol were used.

The proportionate mixtures of addition agents which were found to give the most satisfaction with the eleven electrolytes for the preliminary runs were: 1 g. glue and 0.5 g. fuel oil (as emulsion) per L. of electrolytes; and 1 g. glue, 0.5 g. fuel oil, and 0.5 g. cresol (as emulsion) per L. of electrolytes. The mixture of glue and oil gave better results than glue alone, and the mixture of glue, oil and cresol was more effective than the mixture of glue and oil.

The results of the preceding comparative tests demonstrated that the most satisfactory cathode deposits of tin were produced in sulfate electrolytes which contained 100 g. free sulfuric acid and 5 g. HCl per L., and therefore for the balance of the tests, the two electrolytes, B and D, were used. Electrolyte B contained 60 g. of tin as $SnSO_4$, 100 g. free sulfuric acid, and 5 g. hydrochloric acid (11 cc. of conc. HCl, sp. gr. 1.192) per L.; electrolyte D contained 60 g. tin as $SnSO_4$, 72 g. Na_2SO_4 (an equivalent to form $SnSO_4.Na_2SO_4$), 100 g. free sulfuric acid, and 5 g. hydrochloric acid (11 cc. conc. HCl, sp. gr. 1.192) per L. The addition agents were various proportionate mixtures; the relative amounts which were found to give the most satisfactory results are the following:

Amounts used: Gram per Liter of Sulfate Electrolyte					
Mixture	Glue	Fuel Oil	Cresol	Nicotine Sulfate	Aloin
a	1	0.5	..	..	..
b	1	..	0.5	..	..
c	1	0.2-0.33	0.2-0.4	..	..
d	1	..	0.2-0.4	1-1.33	..
e	1	0.2	0.4	1-1.33	..
f	1	0.2	0.4	..	1-1.5

The tests so far reported were made with a current density of 15 amp. per sq. ft. (1.6 amp. per sq. dm.) with the electrolyte at approximately 23° C. In order to demonstrate the effect of temperature, the two electrolytes, B and D, were heated to 47° C., and addition agents, proportionate mixtures c and d, were added. The effect of heating the electrolyte to 47° was to cause the cathode deposits to form tangled masses of needles, spangles and dendrites. Referring to Fig. 1, cathodes No. 1 and 5 were formed in electrolyte B; and No. 2 and 6 in electrolyte D; the temperature of the electrolytes in which No. 1 and 2 were formed was approximately 23° C. and that of the electrolytes in which No. 5 and 6 were formed was approximately 47° C.

Sixteen typical cathodes were selected and photographed. No. 1 to 14 inclusive were formed in sulfate electrolytes in 24 hr. and No. 15 and 16 in chloride electrolytes in three hours. Cathodes No. 5 and 6 were formed at approximately 47° C. and all of the others at approximately 23° C. The electrolytes and addition agents which were used are given in Table III.

Four series of comparative tests were made with the chloride electrolytes, using the four chloride electrolytes (5, a; 5, b; 6, a; and 6, b). The time of electrolysis averaged two hours, and the addition agents tried were the following in the given proportions:

Amount used: Gram per Liter of Chloride Electrolyte				
Cell No.	Glue	Fuel Oil	Cresol	Cresol Sulfonate
1	1	..	..	..
2	1	..	0.2	..
3	1	..	..	10
4	1	0.2	0.2	..

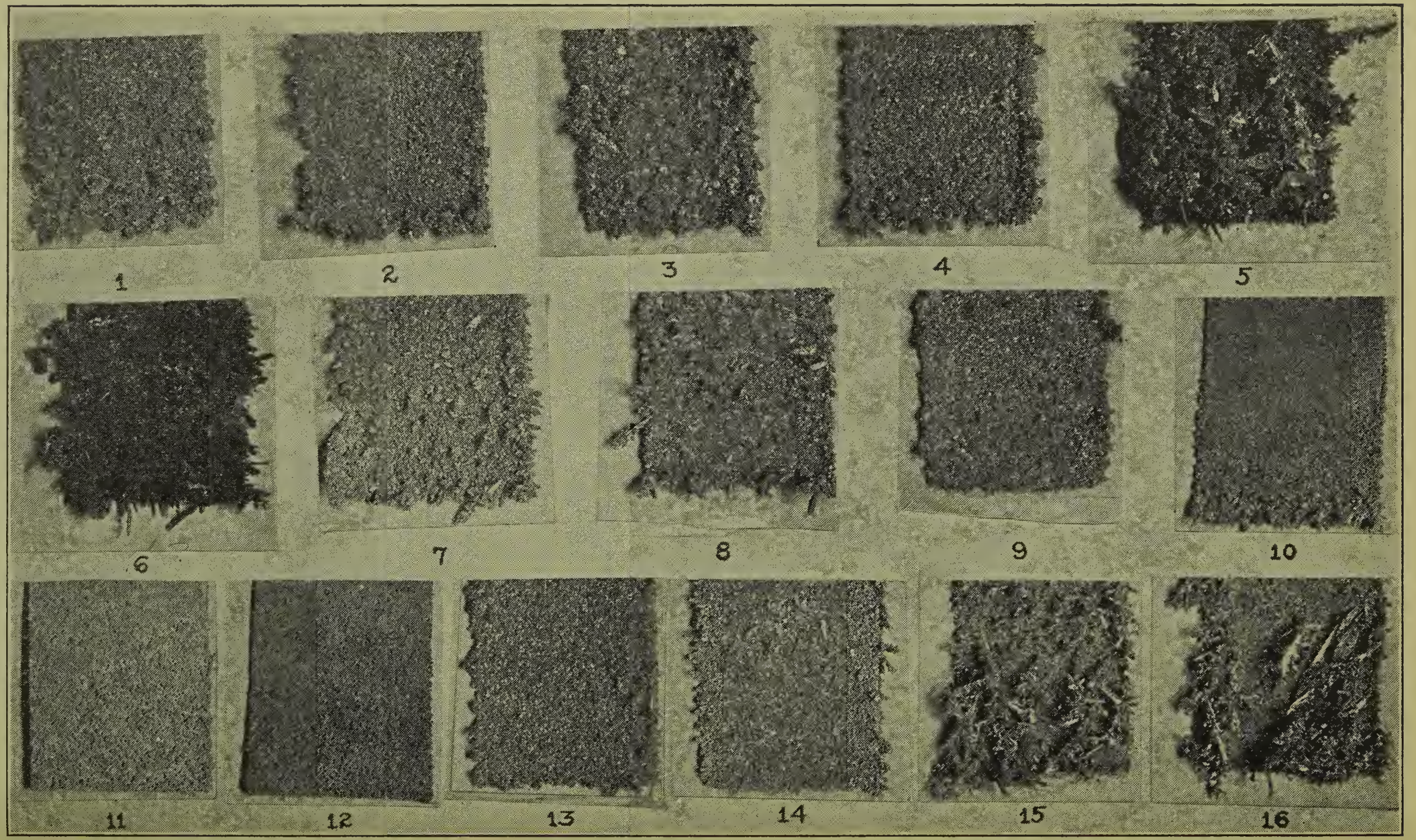

Fig. 1. Typical Tin Cathodes (at a D. C. of 1.7 amp. per sq. dm.).

TABLE III.

Typical Cathodes, Electrolytes in Which Formed, and Addition Agents Used.

Cathode No.	Electrolyte No.	Temperature °C.	Addition Agents: Gram per Liter					Remarks
			Glue	Fuel Oil	Cresol	Nicotine Sulfate	Aloin	
1	B	23	1	..	0.2	0.5	..	(1)
2	D	23	1	..	0.2	0.5	..	(2)
3	B	23	1	..	0.2	1	..	(3)
4	D	23	1	..	0.2	1	..	(4)
5	B	47	1	..	0.2	0.5	..	(5)
6	D	47	1	..	0.2	0.5	..	(6)
7	B	23	1	0.2	0.5	1	..	(7)
8	B	23	1	0.2	0.5	0.5	..	(8)
9	B	23	1	0.2	0.5	..	0.5	(9)
10	D	23	1	0.2	0.5	1	..	(10)
11	B	23	1	..	1	1.33	..	(11)
12	D	23	1	..	1	1.33	..	(12)
13	B	23	1	0.5	0.5	1	..	(13)
14	D	23	1	0.5	0.5	1	..	(14)
15	5, a	23	..	..	..	..	..	(15)
16	5, b	23	..	..	..	..	..	(16)

The cathode numbers correspond to those in Fig. 1.

Electrolyte B contained 60 g. of tin as $SnSO_4$, 100 g. free sulfuric acid and 5 g. hydrochloric acid (11 cc. conc. HCl, sp. gr. 1.192) per L.

Electrolyte D contained 60 g. tin as $SnSO_4$, 72 g. sodium sulfate (equivalent to form $SnSO_4.Na_2SO_4$), 100 g. free sulfuric acid and 5 g. hydrochloric acid (11 cc. conc. HCl, sp. gr. 1.192) per L.

Electrolyte 5, a contained 60 g. tin as $SnCl_2$ (114 g. $SnCl_2.2H_2O$), 59 g. NaCl (equivalent to form $SnCl_2.2NaCl$) and 100 g. hydrochloric acid (22 cc. conc. HCl, sp. gr. 1.192) per L.

Electrolyte 5, b contained the same quantities of tin chloride and sodium chloride as electrolyte 5, a, and 20 g. hydrochloric acid (44 cc. conc. HCl, sp. gr. 1.192) per L.

REMARKS.

1. Dense, coarse grain, nodular.
2. Denser than 1. Good.
3. Similar to 1.
4. Similar to 2. Good.
5. Mass of nodules and dendrites. Poor.
6. Similar to 5. Slightly denser.
7. Bright, compact, fine granular. Good.
8. More crystalline than 7. Fair.
9. Dense, fine crystalline deposit. Very good.
10. Better than 9. Very good.
11. Very compact and hard, light gray deposit. Excellent.
12. Similar to 11. Excellent.
13. Dense, medium granular deposit. Very good. Similar to 9.
14. Dense, fine granular deposit. Some large crystals on edges. Very good.
15. Non-adherent mass of dendrites, spears and needles. Very poor.
16. Similar to 15. Very poor.

All the deposits were so unsatisfactory that no more tests were made with the chloride solutions; the character of the cathodes are shown by No. 15 and 16, Fig. 1. The use of addition agents, such as those above, did not cause the cathode deposit to become denser or more adherent. Due to the poor results with the chloride baths, our tests on addition agents were confined to the sulfate electrolytes.

SUMMARY OF RESULTS.

Sulfate electrolytes are suitable for the refining of tin, whereas the chloride electrolytes are not.

Sulfate electrolytes containing between 40 and 50 grams of tin as stannous sulfate, 75 to 100 g. free sulfuric acid and approximately 5 g. hydrochloric acid (11 cc. conc. HCl, sp. gr. 1.19 to 1.195) or 8 to 10 g. NaCl per L. were found to give the best results. The addition of sodium sulfate in the proportion of 70 to 100 g. per L. of this electrolyte caused the formation of smoother and brighter deposits.

Organic addition agents are essential for the deposition of adherent dense deposits of tin from the above sulfate electrolytes. The use of glue in the sulfate electrolytes in the proportion of 1 g. per L. of electrolyte causes the tin to form denser deposits. The use of mixtures of glue and cresol; glue and nicotine sulfate; glue and aloin; glue, cresol and aloin; and glue, cresol and nicotine sulfate caused the deposits of tin to be smoother and denser than when any one agent was used alone. Even when other addition agents were employed, the presence of glue seemed to be essential, in order to obtain the smoothest, brightest and most adherent deposits.

A well defined quantity of the addition agent is required to produce satisfactory cathode deposits of tin; if an excess is used the tin is deposited as a spongy, non-adherent, amorphous mass; a deficiency gives rise to the more crystalline form of the metal. The proper amount of the addition agent causes the deposition of smooth, dense, bright and adherent tin.

A small amount of hydrochloric acid added to the sulfate electrolytes is beneficial. It not only causes the anode residue to become non-adherent, but it also aids in the formation of more satisfactory cathode deposition; the amount which we found to

be beneficial was approximately 5 g. HCl or 8 g. of sodium chloride per L. of the electrolyte. Larger amounts of chloride cause more crystalline and less adherent cathode deposits. The satisfactory addition agents cause an increase in the cell potential of approximately 0.02 v. Whenever the voltage becomes progressively higher it may usually be attributed to the accumulation of the impurities on the surface of the anode. Cleaning the anodes will cause the potential drop to become normal again.

Small amounts of fuel oil are beneficial when used with glue, cresol, nicotine sulfate or aloin, but are not essential. The proportionate mixtures of the addition agents, which were found to give satisfactory results, are given above in Table III.

Cathode tin deposits formed in the sulfate electrolytes at 23° C. were better than those formed in baths at 47° C.; the deposits at the higher temperature were less adherent and more crystalline. An intermediate temperature may prove to be beneficial.

An increase in free acid in the sulfate electrolytes above 100 g. per L. causes less adherent deposits and the tin crystals to become larger.

Circulation of the electrolyte aids in restraining the long crystal growth and makes the deposit smoother and brighter.

Electrometallurgical Laboratory,
School of Mines, Columbia University,
New York, N. Y., February, 1924.

DISCUSSION.

F. C. MATHERS[14]: I feel that the theory of addition agents as given by Dr. Kern in this paper does not explain all the experimental facts. Glue and cresylic acid (cresol) in the tin sulfate bath produce fine tin deposits, but these same addition agents in the tin chloride bath give only crystalline cathode deposits. I could give other similar examples. Now the theory by Dr. Kern does not consider the fact that the acid ions in a bath have important effects upon the nature of the deposit. In tin plating, the greater the quantity of the addition agents, the smoother and the better the deposit. It is impossible to overtreat the tin solution

[14] Univ. of Indiana, Bloomington, Ind.

with these addition agents. This again is contrary to the theory expressed in this paper under discussion.

E. F. KERN: The effect of an excessive use of an addition agent is detrimental, in that it causes the formation of dark, spongy metal on the cathode. A suitable addition agent causes the metal to deposit on the cathode as finer crystals, which are brighter and more adherent, and as a smoother and denser layer. If the addition agent possesses too highly chemically reducing properties, then the metal is also simultaneously chemically reduced from the electrolyte as non-adherent amorphous metal, or cement, when the current is flowing. The active addition agents are colloids which are attracted to the cathode by cataphoresis, and are adsorbed from the hydrosol film by the metal crystal surfaces. In the case of cresol, it may be added to the electrolyte up to the saturation point; but if added in excess, the undissolved portion will appear as blotches on the surfaces of the anode and cathode, causing uneven deposition of metal on the cathode and uneven dissolving of the anode at the places where the cresol collected.

PER K. FRÖLICH[15]: There is a tendency to divide the action of addition agents into a colloidal effect and a reducing effect. I think it is hopeless to ask any questions about the "colloidal effect" of the problem, since nobody really seems to know what it means. Since Dr. Kern is one of the proponents of the reducing theory, I think it would be interesting to hear how he pictures the mechanism of the reducing action which is said to take place at the cathode.

E. F. KERN: What occurs may possibly be attributed to the combined effect of chemical and electrolytic reduction, and the slow precipitation of the addition agent, accompanied by a slight increase of the potential between that hydrosol film and the outer surface of the cathode, thus throwing out the metal more violently. I hope to submit a paper on the mechanism of addition agents as soon as I have more data.

PER K. FRÖLICH: I know Prof. Bancroft claimed that adsorption was an important factor, but the only attempt to prove this was done by Prof. Mathers, and he did not succeed in doing so.

[15] Research Lab. of Applied Chemistry, Mass. Inst. of Technology, Boston, Mass.

F. C. MATHERS: My theory for the effect of addition agents is that complex ionic combinations are formed in the plating baths. These complexes comprise metal, radical, addition agent and whatever acid radicals happen to be present. This entire complex is deposited on the cathode. Therefore the deposit should differ from that obtained by the deposition of the metal ion alone, or of a complex ion of the metal radical and the acid radical.

The so-called "reducing action" by the addition agent whereby finely divided or spongy deposits are produced can be obtained by certain addition substances and under conditions where any reducing action is unlikely. Small quantities of iodide in the ordinary lead bath produce a finely divided spongy deposit. The glue and cresylic acid, which produce the superior tin deposits, give a spongy deposit in the lead bath. Why would not the action be "reducing" in both baths?

It is difficult to get a theory that will account for all of these experimental facts. I still hold to the idea of the complex cation. I cannot prove it, but I think it is correct.

CARL HERING[16]: In connection with the mechanism of this process, I call attention to a paper that I read before this Society in October, 1906 (Vol. 10, p. 35), in which I described a microscopic investigation. These visible non-electric particles moved with the current and gathered on the cathode surface; when this surface was irregular and the current was reversed, it was interesting to see how the film of these non-electrolytic particles moved away from the cathode, keeping exactly the same shape as the rough surface of the cathode. I also called attention to the fact that some particles move the other way, toward the anode.

W. C. MOORE[17]: Dr. Kern states that glue is the most favorable addition agent. I would like to call attention to the fact that glue is what is commonly known as an *ampholyte*. In this particular case it is an organic substance, which in an acid solution will form salts of an acid, and in a basic solution will form salts of a base; so in a hydrochloric acid solution you might say you had the chloride of glue. I am using that word glue to represent the cathode ion in this particular instance. It seems to me that

[16] Consulting Electrical Engr., Philadelphia, Pa.
[17] Research Chemist, U. S. Industrial Alcohol Co., Baltimore, Md.

the hydrogen ion concentration of these baths would be the most important point in determining whether your glue particles are going to go toward the anode or toward the cathode. In an acid solution you would expect, as Dr. Kern said, that they would go toward the cathode, and in a basic solution you would expect that they would move toward the anode. In that case your glue particles would be more soluble in an acid or alkaline solution than they would be in a solution at the isoelectric point of glue. Really, you may get a deposition of glue particles by the discharge of the charge which they carry, and when they are once deposited it is probably very difficult to get them back into solution. Just as Dr. Hering pointed out, when you reverse the current you would have the glue migrating as a colloidal film, unless you made that solution of sufficiently high concentration, either acidic or basic, in which case the glue would go into solution again and migrate as an ion.

E. F. KERN: In the use of cresol in lead refining electrolytes and in testing *cresol sulfonate* electrolytes, we found that the cresol sulfonate was not the addition agent, but the excess of uncombined cresol which acted as an addition agent. That is, in 1902, a whole series of sulfonates of benzol, phenol, cresol, and naphthol were produced and tested for the electrolytic refining of lead. When cresol sulfonate was used, a slight excess of cresol acted as an addition agent, but it was not so good as glue in the case of the lead; however, less glue was required to produce dense deposits. Insofar as the difference in the character of the electrolyte is concerned, it is known that sodium stannate, which is an alkaline electrolyte, produces non-adherent crystalline deposits, unless sodium cresolate, sodium resinate, or certain soapy materials are present. These were found to be suitable addition agents for alkaline tin electrolytes.

PER K. FRÖLICH: Loeb's theory of the gelatine molecule and its behavior, in combination with Blum's theory of electrodeposition, seems to appear much more helpful in the study of addition agents than all the present hypotheses. It is interesting to note that, except for carbon bi-sulfide in silver cyanide baths, apparently all the effective addition agents known possess electrolytic character. Most of them contain hydroxyl groups and a good

many of them also ammonia groups, so it is not impossible that chemical reactions may take place between the addition agent and some component of the electrolyte. However, it is not likely that metal and colloid is deposited in the form of a complex cation, as suggested by Prof. Mathers, since the ratio of addition agent to metal precipitated is too small to account for this.

C. J. WERNLUND[18]: Dr. O. C. Ralston's views upon the function of addition agents as expressed in his book, "Hydrometallurgy and Electrorefining of Zinc," are worthy of consideration. He believes that the organic addition agents combine selectively with the impurities, and in this way eliminate them in the ionic sense and prevent them from plating out upon the cathode. This agrees with the idea that Dr. Mathers holds as to the effect of addition agents. We have noted the same effect in cyanide solutions. If we use commercial zinc anodes in one cell and electrolytic zinc anodes in another and build up heavy deposits, then we will find that in the commercial anode cell the cathode deposit contains considerable quantities of lead (usually about 0.75 per cent). Furthermore, this deposit is much rougher than the cathode deposit in the electrolytic zinc anode cell. If we now add an addition agent, such as glue or one of the other gums, it smoothens up the deposit of this first cell with the commercial zinc anode. I would like to ask whether Dr. Ralston's ideas are borne out by any other experimental work?

S. SKOWRONSKI[19]: H. A. Guess, about 20 years ago, did some work with a copper bath containing arsenic, and he was able to get a remarkably smooth deposit, free from arsenic, by using a nitrated oil. At that time they were nitrating what was called Hard Oil No. 4 (vaseline), and he recommended it as an analytical procedure. As such, however, the method failed, owing to the deposition of carbon or carbon compound upon the cathode along with the copper.

C. P. LINVILLE[20]: In commercial electrolytic tin refining operations it was found that there is a fairly uniform amount of depletion in the addition agent. In Alexander and Stack's

[18] Research Chemist, Roessler and Hasslacher Chemical Co., Perth Amboy, N. J.
[19] Research Chemist, Raritan Copper Wks., Anaconda Copper Co., Perth Amboy, N. J.
[20] Metallurgist, Calco Chemical Co., Bound Brook, N. J.

paper,[21] before the Institute of Mining Engineers, the statement is made that: "In all tin electrolytes used, the addition agent becomes depleted at a constant rate, varying from 1/3 to 3 lb. (0.15 to 1.8 kg.) of glue, and from 8 to 16 lb. (3.6 to 7.2 kg.) of cresylic acid per ton of tin refined, depending upon the character of the electrolyte used." The point brought up by Dr. Wernlund, referring to the use of colloids to segregate out the impurities from the solution, hardly holds true for tin refining, because the amount of impurity in a tin refining solution has never been found to be appreciable—no other metal being present.

COLIN G. FINK[22]: I do not think that Dr. Kern or anybody else tried to leave the impression that after a colloid particle once fastened itself to the cathode at a certain point it was free to move to some other peak. When we analyze the cathodes we actually find the carbon of the addition agent. Many tons of glue have been codeposited with copper in the electrolytic refining process.

[21] The Reduction and Refining of Tin in the United States. H. H. Alexander and J. R. Stack, Trans. A. I. M. E., Pamphlet edition, p. 31, February meeting, 1924.

[22] Head, Division of Electrochemistry, Columbia Univ., New York City.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, Mr. S. Skowronski in the Chair.

ELECTROLYTIC TIN.[1]

By Charles L. Mantell.[2]

Abstract.

A discussion of the various electrolytic baths for the refining of tin, from the viewpoint of their application on a commercial scale. The advantages, disadvantages and special applications are pointed out, with an exemplification of the reasons for the satisfactory stannous sulfate, sodium sulfate, sulfuric acid electrolyte. A number of literature references are given for the various baths discussed.

Electrolytic tin is a relatively new arrival in the family of pure metals. Its development has progressed in the face of difficulties and opposition, much of which is upon an unfounded basis.

The use of electrolytic processes for the winning of metals from low grade ores, which are too poor in metal content to warrant consideration for smelter charges, but high enough so that by leaching and electrolytic processes large scale operators are able to produce metal at lower production costs than the smelters of high grade ores, is too well known in the case of copper, silver, etc., to warrant any discussion here.

The metallurgy of copper has been worked out in great minuteness and detail; in contrast, the metallurgy of tin is a virgin field. The reason for this state of affairs is not difficult to find. The sole source of tin is the native SnO_2, cassiterite, an ore not at all leachable; totally unlike the carbonate, sulfate and sulfide ores of copper. Stannic oxide is relatively heavy, and can be separated from the ores containing it by mechanical processes of concen-

[1] Manuscript received February 12, 1924.

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tration. This is the only possible method; at the present time no solvent for native stannic oxide is known. The reduction of the oxide thus separated can be effected without difficulty by the use of carbon. The resulting tin can also be refined, to a degree of purity sufficient for most purposes, by ordinary dry methods, such as drossing and liquation. These are simple processes which are entirely satisfactory for the metal resulting from the reduction of pure ores, such as those produced in the Straits Settlements and mines in that vicinity, which produce the well-known Banca and Billiton brands of tin.

The production of pure tin ores, whose source is alluvial, is constantly decreasing. This is the source from which pure tin metal can be most easily produced by straight fire methods. The production of vein ores, such as Bolivian, highly contaminated with undesirable impurities, is constantly increasing to make up for decreases of "stream" or alluvial tinstone, and to produce metal to satisfy the annually increasing demand.

There are many decided drawbacks to the present method of winning tin from its ores. Liquid tin metal and its compounds are extremely corrosive, rapidly destroying by chemical combination almost all materials used as furnace linings or containers. Tin compounds are amphoteric in character; in smelting, if the slag be too acid, tin will be lost as a silicate in the slag; if the slag be too basic, tin will also be lost as a stannate. The tin silicates can not be completely reduced to the metallic state, so that tin metal is actually lost. Appreciable amounts of iron in the ore will cause the formation of hardhead, a high fusing point iron-tin alloy, from which it is difficult to recover tin. By the best metallurgical processes available today only about 90 per cent of the tin in the ore concentrate is recovered as metal.

The tin metal produced from straight metallurgical processes from impure ores is at best a very impure form, containing Pb, As, Sb, Fe, Cd and Cu as impurities, from which it must be refined. The usual methods are by liquation, boiling or tossing. In liquation advantage is taken of the low melting point of tin; impure metal is heated on the inclined bed of a furnace to a temperature just above its melting point, comparatively pure tin trickles down to a basin below, leaving higher melting point

impurities on the bed of the furnace. Liquation will not remove readily fusible lead and bismuth impurities; these are removed by boiling or tossing. Both of these are oxidizing methods, the first is similar to the blowing operation of the copper refinery; the second consists of pouring ladlefuls of molten metal from a height back to the bath of metal. The metal is then allowed to stand in the liquid state for several hours to allow gravity separation of remaining heavier impurities.

From such operations as these it is obvious that a tin metal of a quality equivalent to electrolytic copper or nickel can not be produced. In 1906 Blount[3] was among those to recognize the great desirability of producing electrolytically a purer metal than the commercial pure tin containing 0.50 to 1.00 per cent impurities. In the manufacture of high-grade non-ferrous alloys, particularly bronzes, solders and gun metal, a pure metal is distinctly preferable to one containing miscellaneous alien substances. Nevertheless, in 1906 electrolytic tin had no industrial existence. Throughout the literature since that time until 1917 statements were made that there was no field for the electrolytic process for the refining of tin, as metallurgical processes produced tin in a sufficiently pure condition for ordinary uses, and extremely pure metal had no particular sale.[4]

Seemingly, electrolytic tin must overcome the same series of useless prejudices and adverse propaganda that electrolytic nickel and copper overcame. There is no question that electrolytic refining will produce a purer product than liquation and tossing methods; that the purer metal produced allows the production of higher grade non-ferrous alloys; that many manipulative difficulties in the application of tin metal vanish when the deleterious impurities are no longer present, and that electrolytic processes can be used to obtain pure metal from the decidedly impure or "foul" Bolivian ores, from which straight dry thermal methods of refining produce only a poor grade of metal.

ELECTROLYTES.

Many electrolytes for tin refining have been proposed; some of them have been used on a commercial scale; others have found

[3] Blount, Practical Electrochemistry, p. 124 (1906).
[4] Allmand, Principles of Applied Electrochemistry, p. 287 (1912).

application only for plating, and a multitude of others so violated commercial considerations that they have never been used. In the selection of a salt for any refining process, the following conditions will have weight. The acid radical must be fairly cheap and stable. The salt must be soluble. If impurities are to be taken out as slime, they should be insoluble in the electrolyte used. The tank lining should not be affected by it. Poisonous fumes should not be given off, and the cathode should not readily redissolve.

Plating stands on a little different ground in that it is a quality process. Therefore, the cost of the salt used is not vital, and in small operations poisonous fumes may be controlled.

In the special field of tin refining it is necessary to have an electrolyte in which the tin compounds formed are very soluble. The tin concentration of the electrolyte must be great enough for the current density used. Tin electrolyte must be free from metal ions electropositive to tin, otherwise these metals will plate out with the tin. As in copper refining, the electrolyte must be circulated to avoid segregation and polarization. The use of a warm electrolyte results in lower voltages and more even anode corrosion. A very desirable electrolyte, however, would be one that functioned satisfactorily at room temperature, thus eliminating the necessity of external heating. The presence of suitable addition agents tends to cause smooth, dense, coherent cathode deposits.

Alkaline Sulfide Bath[5]*:* One of the oldest electrolytes used for tin refining is the sodium sulfide bath of Claus and Steiner.[5] This bath was used commercially at Bootle, England, for several years. The electrolyte consisted of a 10 per cent solution of Na_2S with dissolved sulfur; smooth deposits were gotten below 0.2 v., above which H was evolved and spongy deposits formed. Peruvian metal of 93 per cent tin content was refined to a 99.9 per cent material. The electrolyte had to be kept uncontaminated from foreign metals suspended or dissolved; no circulation was possible, as the anode mud would foul the solution. The current could not be interrupted during a run, otherwise the polarization current would oxidize the cathode. The current density was 1

[5] Alkaline Sulfide Bath: Zeit. Electrochem., **15**, 33-6, 63-5; Steiner, Electro Chem. and Met. Ind., **5**, 309-12 (1907); Fisher, Z. anorg. chem., **42**, 63 (1904); Neuman, Z. Electrochem., **27**, 256-68 (1921).

amp./sq. dm. The bath had to be maintained above 80° C.; below 70° C., H_2 was evolved. Sb was deposited on the cathode along with tin at c. d. greater than 0.1 amp./sq. dm. For commercial use, this bath violates too many considerations.

Alkaline Baths: The alkaline baths[6] studied by many workers consisted of $SnCl_2.2H_2O$ dissolved in NaOH. A typical electrolyte is that of Beneker, which consisted of 125 g. NaOH, 50 g. $SnCl_2$ and 75 g. $Na_2S_2O_3$ per L. The alkaline baths tend to produce spongy and non-adherent cathode deposits, the baths are none too stable, oxidizing by the action of the air to stannates and insoluble stannic acids; the anode corrosion is greater than the cathode deposition; the cathode deposits are difficult to handle and cause large losses in melting down to a compact form. The bath is operated at 80° C., with a c. d. of 10 amp. per sq. ft. (1.1 amp. per sq. dm.) With c. d. as low as 2 amp./sq. ft. (0.22 amp. per sq. dm.) a fairly compact cathode deposit may be obtained. Straight alkaline baths are not now used for tin refining, but find application in electrolytic detinning and tin plating.

Mathers and Bell, working with a bath of 60 g. crystalline $SnCl_2$, 60 g. NaOH and 1 g. of an addition agent per liter, found that continued satisfactory deposits could not be obtained even with a c. d. as low as 4.7 amp. per sq. ft. (0.52 amp. per sq. dm.) due to gradual oxidation of the Na_2SnO_2. No satisfactory method of prevention of oxidation or regeneration of the bath was found. Tin anodes in alkaline baths have a decided tendency to acquire passivity, at which time anode corrosion stops.

Acid Baths[7]*:* A number of patents have been granted in various countries for tin refining baths using the tin salts of organic acids, such as acetic, formic, tartaric, citric, oxalic, and the tin salts of phosphoric and boric acids. All of these have the objection that the electrolyte is expensive, easily decomposed, the solutions may be unstable, and the electrolytes must be kept pure. These baths have been found useful for electrotinning, but not at all for electrorefining.

[6] Alkaline Baths: Metal Ind., **14**, 200-1 (1916); Trans. Am. Electrochem. Soc., **29**, 405 (1916); Metal Ind., **18**, 361-2 (1920); Hollard Bull. Soc. D'Enc. L'Ind. Nat., July, 1912; Mennicke, Metallurgie des Zinns; Hughes, Beama, **10**, 138-41 (1922); Mathers and Bell, Trans. Am. Electrochem. Soc., **38**, 135 (1920).

[7] Acid Baths: Mathers and Cockram, Metal Industry, **14**, 252-3 (1916); Pasztor, Le Et. Electrochem., **16**, 281-5; D. R. Pat., 276,181 (1912); Battle, U. S. Pat., 1,202,149; Marino, Brit. Pat., 11,011 (1915); Delahaye, Fr. Pat., 484,148 (1917).

Chloride Baths[8]*:* There have been proposed many baths applicable to tin refining, which make use of the solubility of stannous and stannic chlorides. Among these may be mentioned that of Brand, consisting of about 1 per cent by weight of concentrated HCl and 9 per cent of $SnCl_2$. Neutral or acid solutions of stannous or stannic chlorides produce coarse crystalline cathode deposits. It has been claimed[9] that "beautiful, dense deposits of tin can be obtained without the evolution of H_2 by electrolyzing a NaCl-$SnCl_2$ solution with low current density at ordinary temperatures." This holds true only for a short while; in continuous operation crystals and trees are produced which short circuit the electrodes. The chloride baths have been advocated for use in diaphragm cells; but diaphragms in commercial refining introduce an undesirable cell complication and an increased voltage drop across the cell.

Fluosilicate Baths[10]*:* The successful application of H_2SiF_6 as an electrolyte for lead refining caused workers to attempt to apply the same to tin, a more or less related metal. It was early realized that the addition of small amounts of H_2SO_4 in the bath would prevent electrolyte contamination, by causing the formation of insoluble $PbSO_4$, which rapidly fell out of the solution and became part of the slimes. Some of the laboratory workers on the problem shortly worked out suitable addition agents, without which an entirely satisfactory electrode deposit could not be obtained.

In the first commercial tin refining plant in the United States, that of the American Smelting and Refining Co. at Perth Amboy, N. J., the fluosilicate bath was used. Its composition was about 15 per cent H_2SiF_6 and 4 per cent Sn, with H_2SO_4 added as a lead precipitant. The baths produced metal of 99.96 to 99.98 per cent Sn content. At the Perth Amboy plant the company made its own H_2SiF_6 in the sulfuric acid plant. In one of its

[8] Chloride Baths: (Brand Bath) Schnabel-Louis, Metallurgy, 1907, Vol. II, p. 549; Quintaine, Brit. Pat., 5,496 (1900); Ferth, German Pat., 205,051 (1907); Michaud and Delasson, French Patents, 16,388 and 435,936 (1912); U. S. Pat., 1,124,315.

[9] Bull. Soc. D'Enc. L'Ind. Nat., July, 1912, p. 28.

[10] Fluosilicate Baths: Eng. and Mining Journal, May 17, 1916; Hollis, U. S. Pat., 916,155; Mennicke, U. S. Patents, 779,091 and 779,092; Mathers, U. S. Pat., 1,397,222; A. S. and R. Co., French Pat., 479,569 (1916); Schulte U. S. Pat., 1,423,686; Whitehead, U. S. Pat., 1,157,830; Elec. Rev. West. Electricity, 68, 507 (1916); Voil, Eng. Mining Journal, 101, 927-9 (1916).

British patents[11] the A. S. and R. Company give the bath composition as H_2SiF_6 20 per cent, and H_2SO_4 0.10 per cent. The cathodes in initial operation were enclosed in porous cells. After the solution had taken up 6 per cent of Sn, the porous cells were removed. The voltage across the tanks was then changed from 4 to 5 v. to 0.5 v. H_2SO_4 was added as it was used up, The porous cells used in the first part of the process were supported by glass blocks and by clips on rods from which the cathodes are suspended.

The tin refining plant at Perth Amboy in 1917 consisted of 68 tanks similar in size and construction to those used for copper. The tanks were wood, lined with asphalt coating. The electrolyte was circulated from tank to tank through hard rubber fittings. Each tank in the refinery contained about 11,000 lb. (5,000 kg.) of anodes. The cathode starting sheets were of tin about ⅛ in. (3 mm.) thick, made by casting in a manner similar to the making of thin lead cathode sheets. The c. d. was about 12 amp. per sq. ft. (1.3 amp. per sq. dm.), the metal deposition per amp. hr. being about twice that of copper (theoretical 2.2188 g. per amp.-hr. Sn^{++}). The anode life was about 20 days, and the output of the plant about 15 to 20 tons of tin metal per day. The product analyzed 99.96 to 99.98 per cent Sn, which is purer than the best Straits product. The manufacturers of high-grade tinfoil, tin plate and non-ferrous alloys reported the absence of manipulative difficulties with this pure metal, which difficulties were always more or less present with metal refined by pyrometallurgical methods.

Mennicke in his work on fluosilicate baths obtained excellent deposits by the use of an electrolyte of 10 per cent Sn and 10 per cent H_2SiF_6, operated at 20° C.; c. d. 9.3 amp. per sq. ft. (1.03 amp. per sq. dm.) at 0.4 v. The distance between his electrodes was 2 in. (5.1 cm.) His electrolyte was made by dissolving freshly precipitated $Sn(OH)_2$ in H_2SiF_6. Free H_2SiF_6 was found not to interfere with satisfactory deposition, but the use of anodes containing Pb caused spongy deposits. While the fluosilicate bath functions in a satisfactory manner, it has the disadvantage that it is difficult to prepare, it is none too stable, and the materials used are expensive.

[11] A. S. and R. Co., British Pat., 11,816 (1915).

Sulfate Electrolytes[12]: In the search for baths less expensive than the fluosilicate, workers in the field turned to sulfuric acid as a source of a cheap ion. It was shortly found that electrolytes such as sodium sulfate alone produced spongy non-coherent deposits, and that with sulfuric acid crystalline deposits were produced, which soon short-circuited the electrodes. It is claimed that the cathode deposit can be modified in a satisfactory manner by the use of addition agents, such as gelatin, phenol, phloroglucinol or similar substances. Later work by Schlötter showed the necessity of having the straight sulfate bath free from alkalies and ammonium salts. One of Schlötter's baths has the following composition: 120 g. $SnSO_4$, 2 g. gelatin, per L. Gelatin and cresylic acid soap emulsion as addition agents have temporarily produced satisfactory deposits of tin, but their activity seems to be quickly destroyed.

The sulfuric acid bath becomes inoperative in the case of anodes containing appreciable amounts of lead, say 2 per cent or thereabouts. This is a decided disadvantage in using this bath for commercial tin metal produced from Bolivian ores. When sulfuric acid and sodium sulfate are used together as electrolyte, the tendency of the acid to cause crystalline deposits is neutralized by the tendency of the sulfate to form sponge metal. By properly balancing the proportions of one constituent against the other a coherent, dense cathode deposit, satisfactory for commercial refining, is produced.

Present Commercial Bath[13]: The bath which has proved satisfactory for commercial tin refining at the present time is that of Fink, which has about the following composition: 233 g. $Na_2SO_4 . 10H_2O$, 150 g. H_2SO_4, 35 g. Sn, 2 g. aloin per L. In the case of high lead content anodes, this bath is modified to the following: 60-120 g. $Na_2SO_4 . 10H_2O$, 50 g. H_2SO_4, 35 g. Sn, 2 g. aloin. The Glauber's salts may be replaced by salts such as ferrous sulfate, without greatly impairing the cathode deposit, yet improving the anode corrosion.

This bath has the advantage that high lead content anodes can be refined, the electrolyte is cheap, thick deposits can be obtained

[12] Schlotter, U. S. Pat., 1,426,678; Norrie, Canadian Pat., 211,475; Schlotter, British Pat., 148,334 (1920); Michaud and Delasson, British Pat., 20,557 (1912).

[13] Colin G. Fink, U. S. Pat., 1,466,126.

without treeing, the bath is operative satisfactorily at room temperature, and no heating is required; no diaphragms are necessary, the impurities in the anode form an easily removed sludge, and circulation, with no bad effects but only the desired good ones, is possible and made use of. The addition agent, aloin, is cheap, easily prepared, and remains active for a relatively long period of time. There is present in the bath a preponderating concentration of sulfate ions, and small amounts of chlorine, fluorine, or fluosilicate ions may be present and not be prejudicial to the final result. In addition the electrolyte contains a preponderating concentration of ions more electronegative than tin, such as sodium, and as a result of the refining, magnesium, iron, aluminum, chromium, etc., which will not be deposited in preference to tin because of their more electronegative nature.

The commercial c. d. is 10 amp. per sq. ft. (1.1 amp. per sq. dm.), the voltage being about 0.2. With reduced acid concentration the voltage may increase. Additional metal sulfates, such as those of iron, titanium, cobalt, nickel, manganese and chromium, when added to the tin refining cell, have the beneficial effects of loosening the slimes, which tend to adhere to the anode, thus rendering anode corrosion easier, and of improving the density and hardness of crystals deposited on the cathode.

RESUMÉ

Straight pyrometallurgical methods can not produce as pure tin metal as electrolytic refining. Pyrometallurgical methods do not produce, without difficulty, tin of the desired purity from Bolivian ores.

The alkaline sulfide baths for refining are unstable, will not permit circulation, and have to be externally heated; the same holds true for the alkaline baths, which have the additional disadvantage that anode corrosion is greater than cathode deposition.

The organic acid baths are unstable and expensive, useful only for electroplating; the same holds true for the boric and phosphoric acid baths.

Tin is deposited from neutral or alkaline baths in a finely granular or spongy condition, which deposits are difficult and expensive to handle.

Acid baths give rise to "tree" deposits, which eventually short

circuit the electrodes. Acid baths containing chlorides give rise to very long crystals. Certain organic addition agents, used in this bath, will reduce the size of the cathode crystals, but large quantities of addition agents are required to produce deposits easily handled without mechanical loss. A similar set of conditions hold true for the sulfuric acid bath.

The fluosilicate bath, while producing satisfactory results, is expensive and needs the addition of H_2SO_4 to prevent the deposition of lead along with the tin.

The sulfate bath, such as Na_2SO_4 or $SnSO_4$, tends to give spongy deposits of the same character as those from alkaline or neutral baths.

The combination sulfuric acid-alkali sulfate tin sulfate bath combines the treeing of the acid bath with the sponge deposit of the alkaline bath, by neutralization of one effect by the other, producing a satisfactory medium for commercial electrolytic tin refining.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, Mr. S. Skowronski in the Chair.

ELECTROLYTIC REFINING OF TIN.[1]

By J. R. Stack.[2]

Abstract.

Electrolytic refining of tin has been carried out on a large commercial scale at Perth Amboy, N. J., since 1916. To date, the only practical solution of the problem of separating from tin impurities such as antimony, arsenic, lead and bismuth lies in electrolysis. The various electrolytes tried out commercially are discussed. The treatment of the anode slimes is briefly described.

Electrolytic tin refining, although comparatively new, is no longer looked upon as an experiment. Over 35,000 tons of the metal have been refined into high purity electrolytic tin.

The only commercial electrolytic tin refinery is located at the Perth Amboy plant of the American Smelting and Refining Co. The first installation in 1916 consisted of 68 tanks having a capacity of 250 tons per month. When the success of the process was demonstrated, the refinery was enlarged to 340 tanks, having a monthly capacity of 1,500 tons.

ADVANTAGES OF ELECTROLYTIC TIN REFINING.

The tin produced by electrolysis is extremely pure, and compares favorably in merchantable quality to other brands of pure tin. The major demand for the metal is in the form of pure tin, and the electrolytic process converts the tin obtained by smelting impure concentrates to a pure metal 99.90 per cent Sn or better.

The precious metals are not usually associated with tin in large quantity, but occur in some ores, and if present are recovered from the anode slimes. Tin frequently contains other valuable

[1] Manuscript received March 5, 1924.

[2] Superintendent tin operations, Perth Amboy plant, American Smelting and Refining Co.

impurities, such as bismuth, which is found in certain Bolivian concentrates and is concentrated in the anode slimes.

Most tin concentrates from lode deposits contain varying amounts of impurities, and in order to produce metal of merchantable quality it has been customary to use some form of preliminary treatment before smelting, such as chloridizing and leaching. Although the tin produced is not comparable to the high quality of electrolytic tin, there are certain advantages in the preliminary treatment, such as the removal of iron, which

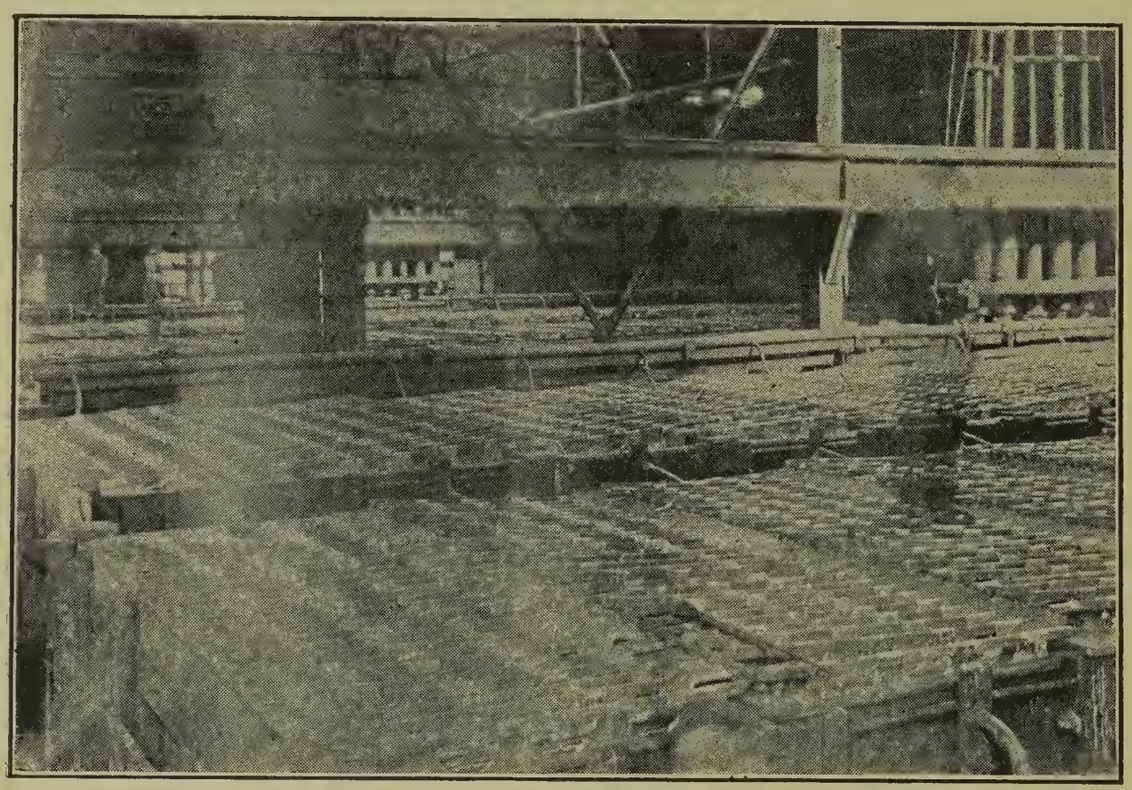

FIG. 1. Tin Refinery.

facilitates the subsequent smelting operation. There is no question in regard to the superiority of electrolytic tin as a metal. Whether or not the electrolytic process will replace the leaching process preliminary to smelting is largely a question of costs. The pure metal commands a premium usually from 0.5 to 1.5 cents per lb. over the price of standard or 99 per cent tin.

IMPURITIES.

The usual impurities to be separated from tin are lead, copper, arsenic, antimony and bismuth. These are all found below tin in the galvanic series of the metals, excepting lead, which is held

in the anode slimes by a precipitating agent in the electrolyte, usually sulfuric acid. Iron is almost entirely separated by liquation before electrolysis. Zinc is rarely found, but has been encountered and when present remains in the solution.

POWER.

The power required to deposit tin is favorable, that is, 8.55 amp. days at 100 per cent efficiency are required to produce one pound of tin. The tank voltage is approximately 0.3, which means that at 85 per cent current efficiency 144 kw.-hr. are required per ton. This figure compares favorably with that used for other metals commonly refined by electrolysis.

TIN ELECTROLYTES.

The process of electrolytic tin refining as developed at Perth Amboy has been protected by a number of patents.[3] The operation of a tin refinery is similar to the operation of a multiple copper tank room, with the exception of the electrolyte composition. Various electrolytes have been used at Perth Amboy with good results. The change was made from one to the other on account of certain advantages gained.

I. Hydrofluosilicic Acid Electrolyte.

This electrolyte was similar to the Bett's electrolyte for lead refining, excepting that a small amount of sulfuric acid was present to precipitate lead. Approximate analysis of electrolyte: Sp. Gr., 1.20; hydrofluosilicic acid, 20 per cent; sulfuric acid, 0.1 per cent; stannous tin, 6 per cent; addition agents, glue and cresylic acid.

Using glue as the addition agent the commercial deposit from this electrolyte was crystalline, although the pilot tank deposits were much superior. However, 48 hr. cathodes could be made without undue loss of efficiency. In October, 1917, the glue-cresylic acid addition agent was introduced with a remarkable improvement in the deposit.

[3] R. L. Whitehead: Electrolytic refining of tin. U. S. Pat., 1,157,830 (1915); H. H. Alexander: Electrolytic refining of tin. U. S. Pat., Appld. Ser., 434,124 (1920); C. P. Linville: Electrolytic tin. U. S. Pat., Appld. Ser., 434,118 (1920); J. R. Stack: Electrolytic process. U. S. Pat., Appld. Ser., 434,114 (1920); J. R. Stack: Process of recovering tin. U. S. Pat., Appld. Ser., 526,871 (1920); F. C. Mathers: Electrolytic refining of tin. U. S. Pat., 1,397,222 (1921).

II. Sulfuric-Hydrofluosilicic Acid Electrolyte.

In December, 1917, the refinery was increased to 204 tanks and the electrolyte changed over to a sulfuric acid base, with sufficient hydrofluosilicic acid to prevent the formation of basic salts of tin. Approximate analysis of electrolyte: Sp. Gr., 1.15; sulfuric acid, 8 per cent; hydrofluosilicic acid, 5 per cent; stannous tin, 3 per cent; addition agent, glue-cresylic acid.

This composition possessed the best conductivity of various combinations of the constituents tried, and the results from this

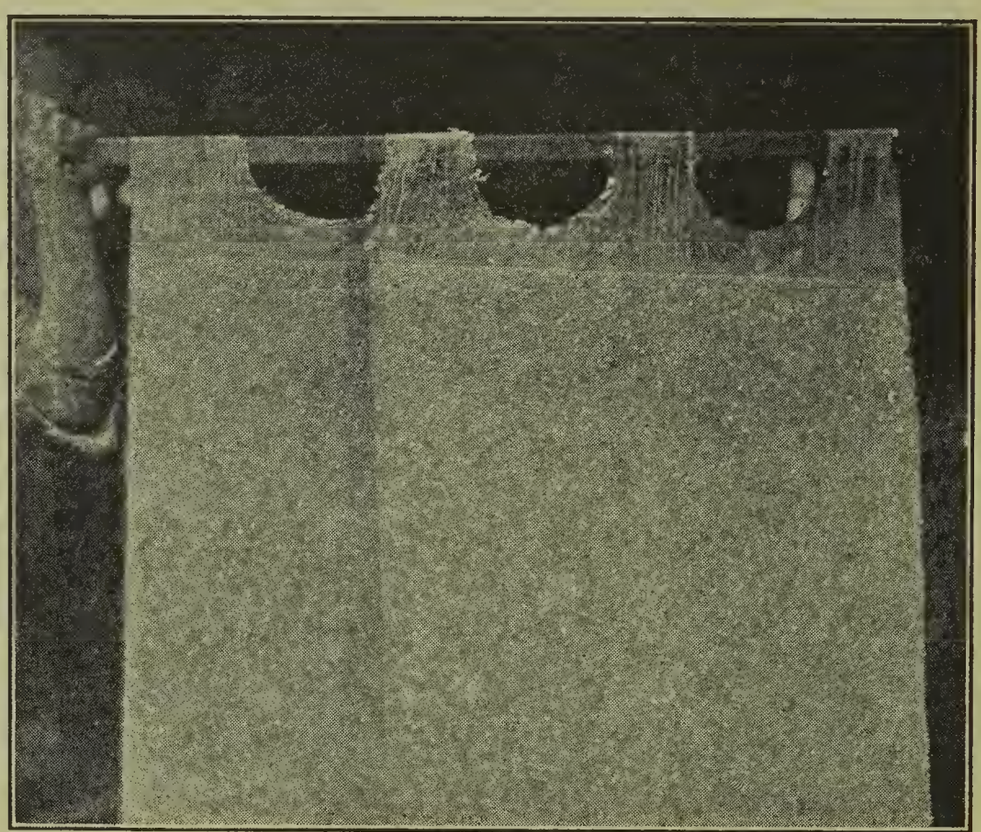

FIG. 2. Tin Cathode.

bath in regard to power, current efficiency, anode corrosion and cathode deposit were satisfactory and superior to the previous electrolyte. With this electrolyte the special equipment required for the high H_2SiF_6 bath, such as hard rubber pipes, mastic lined tanks, etc., could be dispensed with and lead-lined equipment used instead.

III. Sulfuric-Sulfonic Acid Electrolyte.

In January, 1920, a more efficient and cheaper substitute was found in place of H_2SiF_6 in the form of a sulfonic acid of an

aromatic hydrocarbon such as benzol, phenol, cresol, toluene, etc. Sulfuric acid was still maintained as the base of the electrolyte, with sufficient sulfonic acid present to prevent the formation of basic salts of tin. Approximate analysis of electrolyte: Sp. Gr., 1.12; sulfuric acid, 8 per cent; cresol-phenol sulfonic acid, 4 per cent; stannous tin, 3 per cent.

MISCELLANEOUS REMARKS.

In the electrolysis of tin it has been found important to maintain the temperature of the electrolyte at about 35° C. (95° F.) By so doing, more uniform anode corrosion and softer slimes adhering to the anode are obtained.

Occasionally treeing at the cathode occurs, and, if persistent, the addition of muriatic acid has been found beneficial in correcting the deposit. The presence of muriatic acid in quantities in excess of 0.3 per cent greatly increases the effect of the organic addition agent. It was also found that the chlorine ions had a beneficial effect on the anode reactions, bringing about a uniform corrosion or dissolution of the anode and producing a softer and more porous slime. For this reason hydrochloric acid, or a halogen salt, is added to the electrolyte. The amount to be added is limited by the effect which it has upon the cathode deposit. The maximum limit appears to be around 0.3 per cent of chlorine.

The tin is gradually depleted from the solution, due chiefly to the presence of lead in the anodes, and is constantly replaced by circulation of the electrolyte through a Walker basket oxidizer filled with metallic tin.

A definite amount of stannic tin varying from 0.2 to 0.5 per cent is always present in the electrolyte. This is an inert constituent and is carefully watched as a "barometer of trouble," that is, when gradually increasing it indicates poor anode corrosion. When pure tin is dissolved by means of an oxidizer or porous cell no stannic tin is found, but when using impure tin its presence is always noticed.

The current density under normal conditions with 97 per cent tin anodes is 10 amp. per sq. ft. (1.1 amp. per sq. dm.) of cathode surface. The slimes formed adhere for the most part to the face of the anode, and with lower grade anodes the current density

is decreased to obviate the formation of hard slimes, with attending high voltage and "insoluble" anodes.

The problem to obtain soft anode slimes with uniform anode corrosion and to obtain a smooth, dense cathode deposit presented the most difficult obstacles. However, the use of sulfonic acid solved the former, and the glue-cresylic acid addition, the latter.

GLUE-CRESYLIC ACID ADDITION AGENT.

In the electrolytes that have been used on a commercial scale an addition agent has been required to obtain a smooth, dense cathode deposit. Many substances have been tried, and the most efficient one found has been an emulsion of glue and cresylic acid. Its use as an addition agent was first proposed by Prof. Frank C. Mathers, of the University of Indiana, for which full credit is duly acknowledged. The right to use this addition agent was acquired from Professor Mathers, and its value, quantity required and method of use developed at Perth Amboy. The addition agent is constantly depleted during electrolysis, and many evidences corroborate its presence in the cathode deposit. The rate of depletion is about 1 lb. of glue to 8 lb. of cresylic acid per ton of tin refined. Glue alone, or cresylic acid alone, does not function; a mixture of the two is necessary.

The surface tension of the solution is perceptibly increased by the addition agent. According to Betts, "the greater the tension at the surface of an electro deposit, the greater the tendency to keep the new surface forming smooth."

ADDITION AGENT FOR TIN CHLORIDE ELECTROLYTE.

This glue-cresylic acid addition agent does not function in a hydrochloric acid bath. The deposits from a tin chloride bath are more difficult to regulate. However, an excellent deposit can be obtained from a chloride bath by using as an addition agent a mixture of glue and a soluble salt of a metal below tin in the galvanic series, such as copper or bismuth. Just as with the cresylic acid addition agent, glue alone or copper alone does not function, but the presence of both is necessary.

The metal added, such as copper, is eventually found in the cathode, and the deposit remains smooth until this metal has been

depleted; the deposit, however, will continue smooth upon the addition of more of the metal salt at regular intervals. This may be only of academic interest, as the quantity of copper required for tin chloride baths would not produce high purity tin; however, in other electrolytes the quantity of copper required might not sufficiently contaminate the final product to be detrimental.

COLIN G. FINK'S ELECTROLYTE.

Due to the lower price of sulfuric acid, the tendency has been to use a bath essentially composed of H_2SO_4. In this respect, mention should be made of Colin G. Fink's electrolyte.[4] This electrolyte consists of sulfuric acid and sufficient sodium sulfate to prevent the formation of basic salts. This bath was first tried on a commercial scale at Perth Amboy in 1920, and at first did not work satisfactorily on our anodes containing lead. Since then, however, many improvements have been made in order to be able to corrode more impure anodes carrying high percentages of lead.

The analysis of the electrolyte used in the first experimental run is tabulated below: Sp. Gr., 1.10; H_2SO_4, 13.7 per cent; $Na_2SO_4.10H_2O$, 21.2 per cent; Sn″, 1.5 per cent; addition agent, 0.2 per cent aloes (Curaçao).

TREATMENT OF TIN ANODE SLIMES.

The impurities present in the anodes are concentrated fifteen to twenty times in the anode slimes, which have approximately the following analysis: Au, 0.12 oz. per ton (0.0005 per cent); Ag, 130 oz. per ton (0.0546 per cent); Pb, 20 per cent; Cu, 5 per cent; As, 3 per cent; Sb, 5 per cent; Sn, 30 per cent; Bi, 20 per cent.

The slimes must be treated to make the electrolytic tin process complete, primarily to recover the tin and also to obtain any values, such as gold, silver and bismuth, and to eliminate from the process all other impurities, such as lead, copper, arsenic and antimony. Various methods have been used depending upon the composition of the slime material. The two principal ones are briefly outlined.

[4] U. S. Patent, 1,466,126, assigned to Guggenheim Bros., New York, N. Y.

Fusion with Caustic or Soda Ash.

The slimes. essentially finely divided metallic particles, were fused in a cupel furnace, under oxidizing conditions, with caustic soda or soda ash for the removal of tin, arsenic and antimony. Repeated fusions were made by intermittently granulating the crude metal mixing with soda and recharging. The soda slag, containing the arsenic, nearly all of the tin, and part of the antimony, was resmelted and the resultant metal electrolytically refined. The detinned bullion was shipped to the electrolytic lead refinery at Omaha for further treatment and recovery of bismuth.

Electrolytic Treatment.

The slimes were first reduced to metal and cast into anodes, then electrolyzed in an 18 per cent HCl solution using an Electro Filtros diaphragm cell as the cathode compartment. A c. d. of 25 amp. per sq. ft. (2.8 amp. per sq. dm.) was used and the voltage per cell was 2.5 v. The anolyte was kept in constant circulation and heated to about 40° C. (100° F.)

By this treatment, the following approximate percentage of each of the metals present was dissolved, the balance remaining in the anode slimes: Au, none; Ag, none; Pb, none; Cu, 35 per cent; As, none; Sb, 45 per cent; Sn, 90 per cent; Bi, 90 per cent.

As soon as the anolyte became saturated with these metallic salts electrolysis was stopped. The bismuth in solution was cemented out on impure tin, refined by fusion with soda and sulfur, and electrolyzed at Omaha for the production of pure bismuth. The tin was recovered from the solution by precipitation with lime. The anode slimes, high in lead, were smelted to a base bullion, softened and desilverized at the Perth Amboy lead refinery.

SUMMARY.

The electrolytic refining process for tin has been developed as a successful commercial operation. The important features which have contributed to its success have been:

1. The use of electrolytes having a sulfuric acid base, modified by the addition of fluosilicic acid or organic acids, for the purpose of preventing the separation of basic tin salts from the solution.

2. The use of glue-cresylic acid addition agent.

3. The use of small percentages of hydrochloric acid or halogen salt to overcome anodic polarization and assist anode corrosion.

The electrolytic process is the most economical solution of the problem of producing pure tin from the impure Bolivian concentrates or crude metal.

DISCUSSION.

F. C. MATHERS[5]: I think that the reason the fluosilicic acid tin baths were used in the early work was because a better deposit could be obtained from them without glue as an addition agent than could be gotten from the sulfuric acid baths. Perfectly satisfactory deposits could be obtained from the sulfuric acid bath as soon as the use of glue and cresylic acid was discovered and then the use of fluosilicic acid was discontinued.

I have here a tin cathode that was made in my laboratory under better conditions than are demanded in a commercial plant. It is almost an inch thick and is almost as smooth as if it had been cast.

The really wonderful effect of the glue and the cresylic acid can be seen from these three samples which I show you. The first one was made with no addition agents whatever in the sulfate bath. The deposit was spongy. Some glue was added to the same bath and the deposit was still spongy, as shown by this cathode, number two. Cresylic acid was then added to the bath and the deposit was bright and smooth, as shown by the cathode, number three.

C. P. LINVILLE[6]: I, like Dr. Mathers, have a tin sample of which I am proud. Just at the beginning of the period when we were converting our fluosilicate electrolyte into a sulfate-fluosilicate electrolyte, it fell to somebody to carry out a lot of experiments, and I was chosen. We had worked well up to the point where we were satisfied with our electrolyte composition, but we

[5] Univ. of Indiana, Bloomington, Ind.
[6] Metallurgist, Calco Chemical Co., Bound Brook, N. J.

had not been able to get good cathode deposits, when Dr. Mathers came to our aid and suggested the addition of cresylic acid. We then began using his formula for addition agents and my formula for the electrolyte. In the summer of 1917 I arranged a glass cell, hung in a sheet of tin for cathode and a plate of our commercial tin for the anode. Until that time we had never been able to get any tin deposits, running the cells over 24 hours, without short-circuiting. We started this cell and ran it for 18 days, with the result that I obtained this cathode. It is a very good solid cathode, although much more coarsely crystalline than the one Dr. Mathers has shown you. I have also made cathodes that were glass smooth, the edges a little rounded, appearing as though they had been cast rather than deposited. They had a silken finish. That represents the very best that we could obtain, and it was far from what we actually obtained in commercial practice.

It might be well to present the following observations from my notes regarding the commercial requirements of electrolytic tin refining. These notes were based on experience with fluosilicate electrolytes, and later the sulfuric acid electrolytes as modified to meet the plant requirements.

The successful electrolytic refining process for tin demands:

That the impure anodes should corrode evenly and at a high degree of current efficiency; that the solution should be permanent, not altering its composition during long continued use any more than can be helped; that the slimes produced should be soft and non-adherent, and as free from tin as possible; that there should be a minimum of polarization; that the deposition of tin should not be accompanied by cathode gassing; that the deposited tin should be of a high degree of purity, crystalline, dense, bright, and free from trees; that the cathodes should be of such a quality and structure as to make possible a deposition period of from 5 to 7 days without short circuiting.

In order to meet the above requirements, it is essential that: (1) The electrolyte must be such that impurities are not dissolved from the anode and redeposited on the cathode. It must be of such composition as will hold the necessary tin in solution without

any decomposition and precipitation, either in the electrolytic tanks or in the boiling tanks used for concentrating weak wash solutions. It should be as cheap as possible. It should show no change in composition after prolonged use. (2) Polarization must be prevented, and anode corrosion must be even, so that as much tin will be dissolved from the anode as is deposited on the cathode. (3) Circulation must be rapid enough to prevent stratification of solutions.

Electrolyte. The original fluosilicate solution as used by Whitehead was not satisfactory, because it decomposed badly, causing large losses of fluosilicic acid, and it gave trouble by forming insoluble coatings on the anodes interfering with corrosion. Since it corroded lead, it prevented the use of lead-lined tanks, pipe lines, launders, and pumps. A solution of stannous sulfate in sulfuric acid and water is not satisfactory, because it decomposes with the formation of basic tin compounds, especially when the solution is heated. Such an electrolyte cannot be boiled for concentrating wash waters. The electrolyte which I developed overcame the trouble by using sufficient fluosilicic acid (30 g. per L.) along with the sulfuric acid so that no decomposition took place. Stack accomplished the same result by the use of organic sulfonic acids.

Addition Agents. To insure good anode corrosion and prevent polarization, an amount of hydrochloric acid equivalent to 0.2 to 0.3 per cent of chlorine in the solution was used. More than this interferes with the cathode deposition, causing long crystals. For the production of dense cathode deposits, nothing to compare with cresylic acid and glue has yet been found.

Polarization. Under this head is included all those factors which cause high voltage, even though they are not strictly to be classified under "polarization." We have anode polarization and cathode polarization to consider.

Cathode Polarization. This is caused by the deposition of hydrogen on the cathode, thus reducing the area of surface for tin deposition. On account of the higher specific gravity of the

anolyte, there is a great tendency to stratification, and unless the circulation is sufficiently rapid, the upper layers in the cells are apt to be very low in tin, even though the average composition of the cell solution is correct. The presence of addition agents greatly increases the tendency to cathode gassing. I have seen cases where the tin in solution was as low as 8 g. per L. with no indication of gassing, and other cases where gassing occurred with more than 20 grams of tin present. With 40 g. per L. of tin in solution there should be no trouble from this cause.

Anode Polarization. With the high fluosilicate electrolyte, considerable trouble was occasioned by a separation of silica from the solution, and its deposition on the surface of the anode. We do not know the reason for this, but it has not been noticed with the modified electrolytes used in recent years. With stannous sulfate-sulfuric acid electrolytes, a thin film of basic sulfate forming over the anode surface gave trouble. This was remedied when we modified the solution.

Another troublesome film seems to be caused by the precipitation of a thin layer of stannous oxide on the surface of the anode. This forms a very thin adherent coating. A cell set up with pure tin anodes may run along on normal low voltage for a considerable time, and then suddenly the anode will become insoluble and the voltage rise to over 2.5 volts. This condition, even if only partly developed, leads to uneven corrosion, high cell voltage, depletion of tin from solution, high tin in slimes, and tends to give hard dense slimes. Once this condition has been reached it is almost impossible to cure it. It can be prevented by having a sufficient excess of acid present in the solution, along with a small amount of free hydrochloric acid.

Impure anodes, especially those containing a large percentage of lead, give much more trouble than relatively pure ones. It is best to maintain the tin in the anodes above 95 per cent, if possible.

Decomposition of Fluosilicic Acid. We do not know what causes this. It seems to be greater the higher the concentration of fluosilicic acid. The remedy is to keep the concentration as *low* as possible.

Loss of Sulfuric Acid. This occurs only due to the formation of lead sulfate with the lead in the anode.

Loss of Tin from Solution. There are several ways in which this loss may occur. The most important is occasioned by more tin being plated on the cathode than is dissolved from the anode.

Anode Corrosion. With the right composition of electrolyte and other proper operating conditions, anode corrosion is extremely uniform, so that the anode wears down to paper thinness and at all times retains a perfectly smooth surface. With sulfate solutions this is easily accomplished, but the presence of fluosilicic acid interferes and makes it much more irregular. Irregular corrosion is due to coatings over all or a part of the anode. These may be either coatings of silicic acid, stannous oxide, basic tin sulfate, or of slimes. The composition of the electrolyte, as regards excess acid and the presence of halogen ions, seems to be the controlling factor.

COLIN G. FINK[7]: As regards the electrolyte used at Perth Amboy, it is interesting to note the gradual decrease in the concentration of the fluosilicic acid, and the increase in the concentration of sulfuric acid. In our own tests we found that sodium sulfate substituted for the fluosilicic acid not only counteracted all tendency for the tin to hydrolyze, but furthermore did away with polarization so common with the early fluosilicate solutions.

Another point of interest is that the solubility of tin in sulfuric acid, compared to copper, is very low, whereas in the presence of sodium sulfate the solubility of tin increases rapidly as the concentration of sodium sulfate in the acid sulfate solution is increased. Furthermore, dilute acid tin sulfate solutions (wash waters) can be readily concentrated, if sodium sulfate is present, without any hydrolysis taking place or tin salts separating out. We have found that inorganic additions to the electrolyte are very stable as compared with organic additions. To counteract anode polarization in the case of anodes containing 3 per cent and more of lead, we have found the addition of a little chromic acid

[7] Head, Division of Electrochemistry, Columbia Univ., New York City.

to work even better than hydrochloric acid. The lead sulfate film does not adhere to the anodes and cause high voltage if chromic acid is present.[8]

S. SKOWRONSKI[9]: What was the cathode current density on the deposit showed us by Dr. Mathers?

F. C. MATHERS: I really do not remember, but it is about 15 amperes per square foot (1.6 amp. per sq. dm.).

[8] See U. S. Pat. 1,466,126. Aug. 28, 1923. Colin G. Fink. Assigned to Guggenheim Bros., New York.

[9] Research Chemist, Raritan Copper Wks., Perth Amboy, N. J.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, Mr. S. Skowronski in the Chair.

PROGRESS IN ELECTROLYTIC IRON.[1]

By Donald Belcher.[2]

Abstract.

The author sums up the progress made in the electrodeposition of iron in the last seventy-five years. A brief description of the two plants now in commercial operation is given, and a short account of the development work on the Milford process for the hydrometallurgy of iron ores is added.

EARLY WORK.

From the first recorded deposition of iron by Böttger[3] in 1846 to the present day the electrolysis of iron solutions has been the subject of many investigations. Only in the last two decades, however, have there been any important efforts to introduce electrolytic iron as a genuine metallurgical product. It is true that the work of Klein[4], Jacobi[5], Maximowitsch[6] and others, dating back to 1868, had a commercial aspect, inasmuch as these experimenters were successful in depositing a hard and durable coating of iron on the copper plates used for banknote printing. Such work, however, scarcely comes within the scope of this paper, which is concerned with the commercial production of relatively large quantities of iron in one form or another. On the other hand the investigator in no matter what field of electrolytic iron can not afford to overlook this early work, particularly

[1] Manuscript received February 15, 1924.

[2] Chemical Engineer, Milford Electrolytic Iron Co., Milford, Conn.

[3] R. Böttger, Ann. d. physik. u. chem., **67**, 117 (1846).

[4] Klein, Soc. d'encouragement, 1868, 286 and Russ. Pat. 2456 (1869).

[5] Jacobi., Bull. Acad. des sciences de St. Petersburg, **13**, 40 (1868).

[6] Maximowitsch, Z. Elektrochem., **11**, 52 (1905).

that of Alexander Watt[7], Hicks and O'Shea[8] and Amberg.[9] The important researches up to the end of 1920 have been ably reviewed by W. E. Hughes.[10]

Burgess and Hambuechen. In 1904 Burgess and Hambuechen[11] gave the results of their extensive attempts to refine iron electrolytically. Their most satisfactory results were obtained with a solution of ferrous and ammonium sulfates; the cathode current density was 6-10 amp. per sq. ft. (0.7-1.1 amp. per sq. dm.), the cell voltage was slightly less than 1 v. at 30° C., the anodes were ordinary grades of wrought iron and steel. They were able to get deposits as thick as 0.75 in. (1.9 cm.) at nearly 100 per cent current efficiency. They estimated that the refining costs would not exceed $10 per ton of electrolytic iron ready for remelting. These estimates make no provision for interest on the investment, nor do they give any figures on anode consumption.

This work of Burgess and Hambuechen led to considerable speculation and further investigation on the part of others. The possibilities of such a process attaining commercial importance elicited the enthusiasm of the late J. W. Richards. The only practical result of all this interest seems to have been the electrolytic refining plant of the Western Electric Company, at Hawthorne, Ill. This plant uses the process of Burgess as modified by Watts, and will be written of in more detail later.

In 1918 there was a journal notice[12] to the effect that a French company had installed the Burgess process, with the intention of an ultimate production of 25 tons per day, but the writer has neither seen nor heard more of it.

Cowper-Coles. At about the same time that Burgess and Hambuechen were studying the refining of iron in America, Sherard Cowper-Coles[13] was busy with the same problem in England. His electrolyte consisted of a 20 per cent solution of

[7] Alexander Watt, Electrician, 1887-88.

[8] Hicks and O'Shea, Electrician, 1895, 843 and Z. Elektrochem. **2**, 496 (1895).

[9] Amberg, Z. Elektrochem., **14**, 326 (1908).

[10] W. E. Hughes, Trans. Am. Electrochem. Soc., **40**, 185 (1921).

[11] Burgess and Hambuechen. Trans. Am. Electrochem. Soc., **5**, 201-7 (1904).
Stahl u. Eisen, **2**, 789 (1904).
Chem. Ztg., 1904, p. 540.
Elektrochem. Zeitschr.,**11**, 76 (1905).
Iron and Steel Mag., **8**, 48 (1904).

[12] Anon., J. four electrique et electrol., **27**, 89 (1918).

[13] W. Heym., Elektrochem. Z., **16**, 77, 105 (1909).

sulfo-cresylic acid, saturated with iron. He aimed at the production of finished sheets and tubes, and therefore deposited on a rotating cathode. He employed 100 amp. per sq. ft. (11.1 amp. per sq. dm.) at 70° C., and charged his solution with suspended iron oxide. He occasionally added carbon bisulfide. He also worked with chloride solutions and the reader is referred to the report of Palmaer and Brinell[14], who investigated the process of Cowper-Coles.

The present writer confesses that he can not visualize the commercial success of processes using such mixed solutions, and he is inclined to doubt the purity of the iron that could be thus made. For similar reasons he feels that the work of Archibald and Piquet[15] on the deposition of iron from organic solvents can be dismissed from commercial consideration.

The processes of Cowper-Coles do not seem to have attained much importance, although it is believed that Cowper-Coles claims that his researches are the basis of the commercial plant at Grenoble, France, which will be described later.

Fischer and Langbein-Pfanhauser. Another important development has been that of Fischer and the Langbein-Pfanhauser Company[16] in Germany. The inventors used a concentrated solution of ferrous and calcium chlorides at 90° C., or above, and they claim that it can be used at current densities as high as 200 amp. per sq. ft. (22.2 amp. per sq. dm.) In its essentials, this process was used quite extensively during the war by the Germans[17] to provide a substitute for copper in shell bands. It is said that three plants made iron in this way, but no details seem to have been published. The ferrous-calcium chloride bath has been carefully studied by Hughes.[18]

Boucher and Bouchayer. Another process, and by all means the most important to date, is that of the Société "Le Fer," at Grenoble, France. This process, the invention of Boucher[19] in

[14] Palmaer and Brinell, Met. Chem. Eng., **11**, 196 (1913).

[15] Archibald and Piquet, Trans. Roy. Soc. Canada, II, III 107-12 (1917).

[16] Fischer-Langbein, D.R.P. 1908, 212,994; D.R.P. 1909, 228,893; D.R.P. 1910, 230,876; English Pat. 25,092 (1910).

[17] Anon., Elektrochem. Z., 42, 138 (1921).

[18] W. E. Hughes, Bull. Dept. Sci. and Ind. Research (British) No. 6, 50 pp. (1923).

[19] Boucher, Brit. Pat., 28,746, 1910; U. S. Pat., 1,086,132, 1914.
Boucher and Soc. Anon. "Le Fer," French Pat., 458,294, 1912.
Soc. Anon. "Le Fer," French Pat., 446,614, 1911; Brit. Pat., 170,571, 1921.

1910, has been put into successful commercial operation by Bouchayer and Viallet. It has been variously described by Guillet[20], Escard[21] and Bouchayer[22], but the following description has been largely taken from private and unpublished reports made for the Milford Electrolytic Iron Company.

The Bouchayer process consists of refining cast iron, using a hot concentrated solution of ferrous chloride. The iron is deposited in the form of a thin tube on a rotating steel mandrel, which serves as cathode. The electrolyte is circulated rapidly, and before returning to the cells is passed over iron turnings to insure neutrality. It is said that the iron turnings act as a filter also. The patents claim that the noxious effect of the hydrogen liberated at the cathode is overcome by the "oxychloride" of iron which the solution carries. This "oxychloride" was formerly made by aerating the solution in the scrap tanks, but is now said to be formed by a slight electrolytic oxidation of the solution, using an insoluble anode.[23] The plant now consists of 2 rows of 30 cells, each row forming a separate electric circuit, at 100-130 v. Each cell takes from 3 to 4 v., depending on the state of the anode and the size of the cathode; 1,000 amp. are used in each circuit. Since the same current is used for all cells, regardless of mandrel diameter, the cathode current density varies, but averages about 70 amp. per sq. ft. (7.8 amp. per sq. dm.) The cathode current efficiency is close to 100 per cent.

The mandrels are 4 m. long, and vary from 85 to 160 mm. in diameter. They are rotated at various speeds, according to the diameter; the 160 mm. mandrel has a speed of 180-200 r. p. m.

The anodes for each cell consist of 2 L-shaped castings. The electrical connection is made at the top, near the center. The anode is left in the cell until the electrical connection fails. The writer has seen no exact figures for the consumption of these anodes, but believes that not over 80 per cent is actually dissolved in the cells.

The mandrel rests on wooden bearings and is driven through a pin-coupling; the electrical connection is made by mercury.

[20] Guillet, Iron Age, **94**, 1390-1 (1914); Rev. Met., **12**, 81-94 (1915).
[21] Escard, Iron Age, **105**, 732 (1920); Genie Civil., **75**, 165-71, 199-201, 225-226 (1919)
[22] Bouchayer, Genie Civil., **82**, 503 (1923).
[23] Brit. Pat., 170,571 (1921).

Space does not permit of a detailed description of the driving and electrical devices.

The temperature of the electrolyte is 70-75° C. Some trouble is experienced in maintaining this temperature. The feed pipes are indifferently insulated; the cells have light wooden covers. It is understood that a still higher temperature would be desirable.

The electrolyte is made up of scrap iron and commercial hydrochloric acid. It contains 24 per cent by weight of iron, and has a specific gravity of 1.5. None of it is discarded. It is not known whether any addition agents are used. The solution is electrically heated in the feed tanks by 3-phase alternating current supplied through graphite electrodes.

The thinnest tube made is 2 mm. thick; the thickest, 5 mm. The tubes are not perfectly uniform; this depends on the state of wear of the wooden bearings. With new bearings the mandrel runs truly and the deposit is relatively uniform.

When the mandrels are removed from the cell they are placed in a slow-speed lathe, which carries a travelling double gas jet, which suffices to remove enough hydrogen so that the tube may be stripped without cracking. This stripping is done in the same lathe, by compressing the deposit by means of three travelling rolls which are hydraulically forced against the deposit. This pressure suffices to expand the iron circumferentially, so that the tube becomes entirely loose from the mandrel. The tube is then given a thorough anneal in an open flame continuous furnace.

After the tube is removed, the mandrel is scoured and polished and then placed in a bath of lead perchlorate with lead anodes. Here the mandrel is given a light coating of electrolytic lead. It is thought that this is done for two reasons: (1) To protect the mandrel from rust, and (2) to facilitate the stripping by the presence of a soft, easily fusible layer between the steel mandrel and the iron deposit.

The product of the Grenoble plant goes chiefly into specialized radiator work, where tubes of high ductility are needed. The iron is readily drawn into complicated shapes and is easily welded. The scrap of the plant is used for welding purposes.

The present production is said to be 2 tons per day. Despite

its small capacity, the Grenoble plant is said by competent observers to be genuinely commercial, requiring little labor and superintendence, and producing a high percentage of perfect tubes day after day. A great many years of research and development preceded this accomplishment. It seems that little has been done along the line of boiler tubes although some tests have been made.

The Western Electric Plant. Another important development is that of the Western Electric Company, at Hawthorne, Ill. This work has been described in detail by McMahon[24], and by Speed and Elmen.[25] The plant is an iron refinery, starting with anodes of the following percentage composition: C 0.060; P 0.05; Si 0.23; Mn 0.30-0.50; S 0.10.

The cathodes of cold-rolled steel receive a 0.25 in. (0.64 cm.) deposit of iron of the following percentage composition: C 0.014; P 0.013; Si 0.028; Mn 0.029; S 0.003.

The electrolyte is a mixture of ferrous sulfate and ammonium chloride. The bath is kept at approximately room temperature; the current density at the cathode is 12-15 amp. per sq. ft. (1.3-1.7 amp. per sq. dm.); the e. m. f. is about 1.3 v. The cathode current efficiency is 90 per cent. The electrolyte is continuously circulated and filtered with the aid of Filter-Cel. Traces of glue are used to reduce treeing.

The iron as deposited is very brittle, and thus is readily ground to a fine powder. It is then tumbled with zinc dust and compressed into magnets for telephone work. Such magnets have a high permeability and low hysteresis loss, while the fine state of division of the iron plus the zinc coating cuts down the eddy currents.

This plant produces 2 tons of iron per day. It represents a useful and ingenious development in electrolytic iron, but is not likely to grow into large tonnages.

BUILDING UP WORN PARTS.

The reclamation of worn or undersized parts by applying an adherent coating of electrolytic iron commenced in England and

[24] McMahon, Chem. Met. Eng., 26, 639-41 (1922).
[25] Speed and Elmen, Trans. Am. Inst. Elec. Eng., 40, 596-609 (1921).

France during the recent war. Those most concerned in this development seem to have been Hughes[26] and McFadyen[27] in England, and Kellogg[28] in America. As the writer understands it, there is no attempt to make a thick continuous coating. When a thick coating is needed it is made up of successive thin layers, the surface of each layer being ground and carefully treated to receive the next coating.

The process is one of refining, soluble anodes being used. Both chloride and sulfate baths have been used. The main problem seems to have been to obtain an adherent coating. That this has been remarkably well accomplished is shown by the fact that built-up parts may be hammered, bent and twisted without the least breaking away of the deposit. Visitors to the last chemical exposition in New York City will recall the electrolytic iron exhibits of the Westinghouse Company. Recently that company has opened a sort of "clinic," to which worn or undersized parts may be brought for building up.

Here again is an interesting and valuable commercial advance, but not one which can conceivably grow out of the pound scale.

THE MILFORD ELECTROLYTIC IRON COMPANY.

In 1919, C. P. Perin, while engaged in some work for the British government, visited the Bouchayer plant at Grenoble. It occurred to him that electrolytic iron might be made directly from the ores. The thought led to a few months' small-scale research work at Cambridge, Mass. In brief, the flow sheet which was worked upon was: The solution of finely-ground oxide ores (hematite or limonite) in dilute hydrochloric acid, the reduction of the ferric salt thus formed to ferrous by using SO_2 gas, the electrolysis of the ferrous solution using insoluble anodes. The cathodic iron was to be the product of the plant, the ferric chloride formed at the anode being reduced by SO_2 to ferrous chloride with the production of free acid, the resulting acid solution being used to leach more ore. Many technical diffi-

[26] W. E. Hughes, Electrician 87, 640-2 (1921); Beama 8, 425-31 (1921); Trans. Am. Electrochem. Soc. 41, 317 (1922).

[27] MacFadyen. Trans. Far. Soc., 15 Pt. 3, 98-133 (1920).
J. Soc. Chem. Ind., 30, 113A (1920).
See also Thomas, Automotive Ind. 43, 418-20 (1920).

[28] Kellogg, Min. and Met., Feb., 1922.

culties developed, and it was decided that such a flow-sheet, while not at all impossible, was not particularly attractive. The direct solution in ferric chloride of pyrrhotite, the iron ore of approximate formula Fe_7S_8, was tried and found encouraging. Six months were devoted to work along these lines, in conjunction with considerable experimentation on the production of thick, smooth tubes from chloride solutions. The complexity of the problem was such that work of this duration and scale could do no more than open up the field and show the main line of attack. The culmination of these investigations was the experimental plant of the Milford Electrolytic Iron Company, Milford, Conn.[29]

The Experimental Work at Milford.

A simplified flow sheet of the Milford process for a copper-bearing pyrrhotite is shown in Fig. 1. For lack of space the following description of the Milford experiments must be confined to an outline of the main results obtained, and details must be left for a later paper.

Leaching and Ores.

The Milford leach house was originally laid out to treat 2.5 tons of ore per 24 hr., which would yield about 1 ton per day of electrolytic iron. The plan was to electrolyze a solution of ferrous chloride bearing 180 g. Fe per L., regulating the flow in such a manner as to remove 36 g. per L. of iron at the cathode and thereby produce an anolyte which would have the composition: 72 g. Fe″ and 72 g. Fe‴ per L. It was proposed to treat the pyrrhotite of the Smith mine (Quebec), which had the following approximate analysis (in per cent): Fe 48.5; S 33.4; Cu 1.1; Zn 1.6; SiO_2 3.0; Al_2O_3 1.2; $CaCO_3$ 8.1; H_2O 0.1; traces of As, Ni, Mn, Pb and Mg.

The leaching cycle, which was to be continuous and countercurrent, was divided into two steps. In the primary leach the fresh ore, entering the system, met a weak anolyte, of composition 10. g. Fe‴ per L. When this leach was completed the solution

[29] Perin and Belcher, Min. and Met., Dec. 1921, p. 17.
F. A. Eustis, Chem. Met. Eng., **27**, 684-5 (1922).
Bradley Stoughton, Chem. Met. Eng., **26**, 128-31 (1922); Iron Age, **109**, 32-6 (1922).
Kreutzberg, Iron Trade Rev., **73**, 595-8 (1923).

was completely reduced to the ferrous state. The pulp passed to a Dorr thickener. The overflow from this thickener went to scrap iron tanks, where copper was cemented out and thence to storage. The thickened ore passed to the secondary leach, where it met the strong anolyte (72 g. Fe‴ per L.) coming from the cells. Here the solution was reduced from 72 to 10 g. Fe‴ per L. and the ore substantially depleted of iron. This pulp was settled in a Dorr thickener. The overflow went to the primary

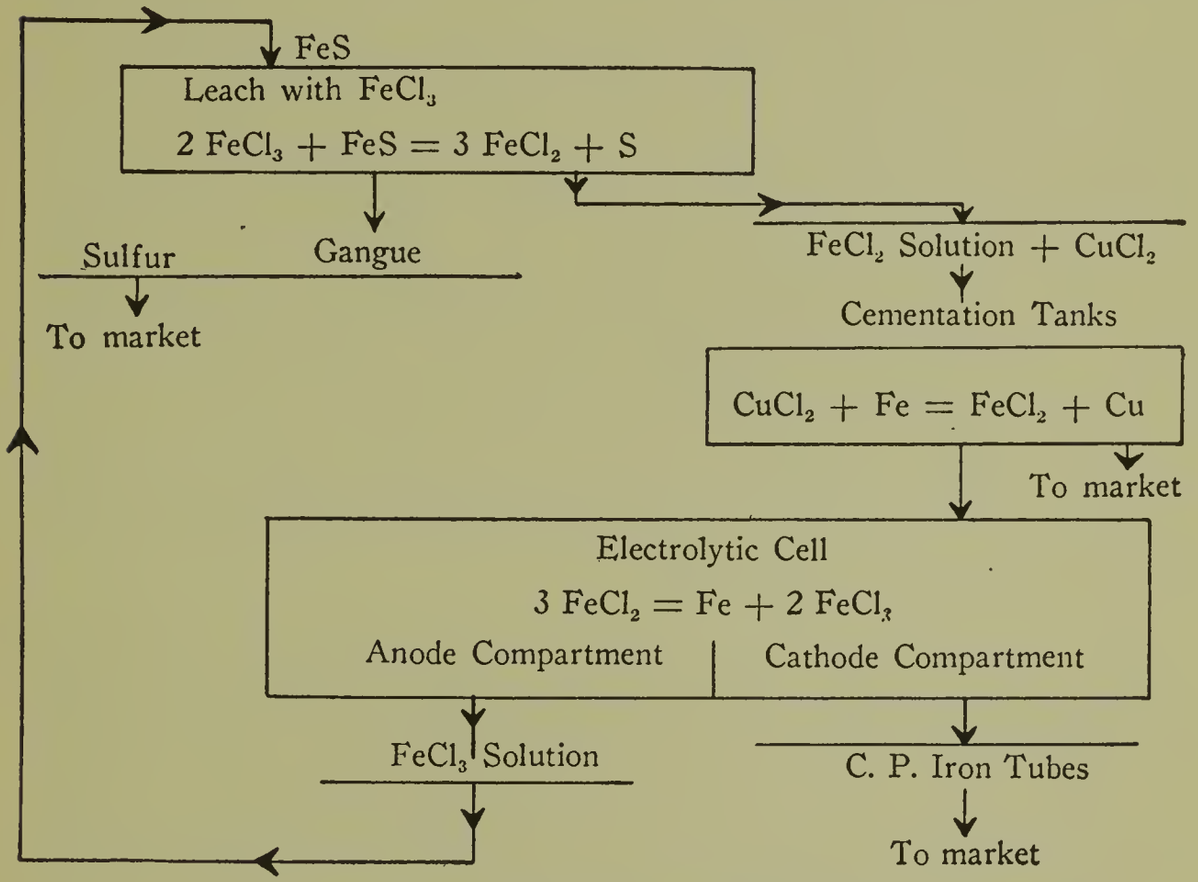

Fig. 1. Flow Sheet of the Milford Process.

agitators; the underflow to a box filter. No provision for separating gangue from sulfur was made at Milford.

Preliminary leaching experiments had shown that with the ore ground to pass 200 mesh, and with the solution kept at 95° C., the primary leach could be accomplished within 2 hours and the secondary within 6 hr. The plant was accordingly laid out on this basis. It was soon found, however, that it was difficult to keep enough cells in operation to produce 1 ton per day, and the leaching system was reduced to one-third of its original capacity. But even on this scale the cells could not be made to

keep up a continuous stream of hot ferric chloride to the leaching system, so that the latter never operated continuously for a long enough time to reach any sort of equilibrium. So in point of view of temperature, regulation of flows and collection of impurities, the Milford leach house, it may be frankly said, furnished no definite quantitative data.

Plenty of mechanical troubles were encountered, most of these resulting from the highly corrosive action of hot ferric chloride. The tanks and cell bodies were all of wood, and this has been found to be a totally unsuitable material, even for solutions of ferrous chloride alone. Bitumastic coverings were found unsatisfactory. Iron piping is out of the question for handling ferric chloride, and not desirable for ferrous. Rubber and ceramic ware seem to be the most suitable. For cells and tanks special concretes, concrete protected with molten sulfur, or some of the sulfur-coke mixtures now being developed, must be used. Pumps gave a great deal of trouble, and recourse was finally had to Antisell pumps of ceramic ware. The leach house should be built lower than the cell room so that the strong ferric may flow by gravity. The agitators were of the Devereux type and kept the ore in suspension very well.

With regard to impurities it has been found that the carbonates of lime and magnesia, and the sulfide of zinc, leach more readily than iron sulfide. If no precautions are taken these three elements will build up to a high concentration in the electrolyte. Calcium and magnesium are harmless in the electrolyte, but they represent a continual loss of effective chloride. It has been found that a preliminary wash of the ore by cold and very dilute sulfuric acid will practically rid the ore of carbonates without appreciable attack on the iron sulfide. With regard to zinc, its presence in the electrolyte means also its presence in the deposited iron. It has been found possible to eliminate all but a small amount of the zinc in solution, by the addition of calcium sulfide, but as the process stands today there is no practicable method of preventing zinc to the extent of about 0.02 per cent appearing in the deposited iron.

The calcium sulfide treatment has been found even more effective in precipitating lead, nickel, cobalt, arsenic and antimony.

The question of impurities has been by no means completely solved, but long strides have been made toward solution.

It is a well known metallurgical fact that pyrites can be converted into pyrrhotite by distilling sulfur from the former. Considerable work was done along these lines at Milford, of which details can not be given here. Suffice it to say that such a conversion is perfectly practicable, and that the artificial pyrrhotites thus formed leach as readily, and in some cases much more readily, than the natural ores.

Cells.

It was the original intent at Milford to make a thin tube of electrolytic iron, which could be stripped and cut into a spiral coil for cold-rolling. Therefore the plant was provided with two wooden cells designed to carry a mandrel 12 ft. long and 12.6 in. in diameter (3.6 m. x 32 cm.) At 55 amp. per sq. ft. (6 amp. per sq. dm.) in 22 hr. this mandrel would receive a deposit about $\frac{1}{16}$ in. (0.16 cm.) thick, weighing 100 lb. (45 kg.) With practically no data upon which to base a design, it was not surprising that these cells did not operate well. The principal troubles were with the driving mechanism and the device by which current was supplied to the mandrel. The operation of these cells was not sufficiently continuous to give accurate electrochemical data, but even a few runs indicated the solution of many mechanical difficulties.

Practically all the valuable data obtained were from the operation of the small rotary cells, which will be mentioned later.

It is well known that the Milford process requires a diaphragm cell. The only suitable material for a diaphragm has been found to be asbestos cloth. The adjustment and maintenance of this cloth in large cells, undergoing continual modification, was expensive and slowed up operations. Therefore, in order to keep the leaching system in operation, attention was turned to the simpler plate type of cell, in which there would be no moving parts.

A plate cell had been designed for the plant, which consisted of a rectangular wooden tank grooved to take the diaphragm frames. The cathodes were steel plates clamped between copper bars; the anodes were slabs of graphite similarly held. This cell was

inoperative because, owing to the swelling and disintegration of the wood, the diaphragm frames could not be removed and the cell could not be repaired. This led to a cell built much like a filter press, with the asbestos diaphragm filling the role of the filter cloth. Two such cells were built and operated with much more success than the first cell. But the wooden frames disintegrated and leaked, and the whole cell had to be taken apart to make the smallest repair. However, a good many hundred pounds of iron were made in these cells. Some of the sheets were smooth, some badly treed. The iron generally was of high purity, averaging perhaps 0.004 per cent S. It is impossible on a stationary cathode to make iron smooth enough for rolling into sheets; the product of the plate cell must be remelted or used in the fashion of The Western Electric Company, as a powder.

The great progress, electrochemically and mechanically, was made on small test cells, of which about six were made and operated. These cells had horizontal mandrels 1 ft. long and 3.75 in. diameter (30.5 x 9.5 cm.). On these cells was worked out the design of stuffing-box, drive, and electrical contact. These designs are not complete and final, but they can be introduced into full sized cells with expectations of reasonable success.

An encouraging design of a plate cell, in which the cathode sheet hangs in a bag of asbestos cloth, has been made but not put into operation.

The many electrochemical facts brought out cannot be detailed here, but may be briefly summarized as follows:

Summary of Facts Observed.

1. The cathode must be clean and free from surface defects. A ground surface is preferable to a turned surface.

2. The slightest interruption of the current causes a lamination in the tube.

3. The presence of any considerable amount of ferric chloride in the cathode compartment (due to defective diaphragm) leads to (a) low current efficiency (b) cracking and peeling (c) in the case of a plate cell to curling of the iron.

4. The higher the acidity of the electrolyte the lower the cur-

rent efficiency. But the acidity can be varied from neutrality to 0.1 normal without injury to the deposit.

5. Turbid solutions do not spoil the deposit. Indeed, due to oxidation, the catholyte is always quite turbid.

6. If the solution is not filtered after leaching, small quantities of divided sulfur are carried over. This sulfur does not injure the smoothness of the deposit but it promotes cracking and gives impure metal. The simplest type of filter remedies this.

7. No organic addition agent has been found to improve the deposits; in fact most of those tried were definitely injurious.

8. Generally speaking the higher the temperature in the cell, short of boiling, the better the deposit. There seems to be nothing critical about the temperature however, and good tubes can be made at as low as 70° C.

9. Concentration does not appear to be important, since perfect tubes were made at Milford at concentrations ranging from 75-275 g. Fe per L., other factors remaining constant.

10. A peripheral speed, measured on the mandrel surface, of 250 ft. (76 m.) per min. is sufficient for 100 amp. per sq. ft. (11 amp. per sq. dm.)

11. Fully 90 per cent of the work at Milford was done at 100 amp. per sq. ft. (11 amp. per sq. dm.) cathode current density. Perfect deposits were made at as high as 275 amp. per sq. ft. (31 amp. per sq. dm.). Generally speaking the higher the current density the finer-grained the deposit and the less brittle.

12. The rotating cathode must be kept well submerged or cracking will occur.

13. Unlike electrolytic zinc, electrolytic iron is not sensitive to inorganic impurities in the electrolyte in amounts far exceeding the concentrations to be expected if reasonable purification is employed.

14. Cathode current efficiencies of 85-90 per cent can be depended upon.

15. With proper cell design anode current efficiencies of 95-100 per cent may be expected.

16. There is no appreciable attack on carbon or graphite anodes.

17. The problems of annealing and stripping have been largely solved and their complete solution for a given set of conditions is a relatively simple matter.

18. There are some obscure changes in the electrolyte, which affect the physical condition of the deposit, which are not yet understood. The question of control of the electrolyte is one which requires further experimentation.

19. A scraper or rubber held constantly in light contact with the deposit as it is being formed is practically a panacea for all electrolyte troubles. Could such a device be worked out on a sound commercial basis the production of smooth, flawless tubes would be solved.

20. The cell voltage at a given current density is mainly dependent on spacing. On a rotary cell with U-shaped anode, the best design, will give a voltage of 3.5-4.0 v. for 50 amp. per sq. ft. (5.5 amp. per sq. dm.) and 4.5-5.0 v. for 100 amp. per sq. ft., (11 amp. per sq. dm.). On a plate cell, which is limited by treeing to about 25 amp. per sq. ft., the voltage should be 2.75-3.00 v. at that current density.

21. It is rather remarkable that a process which treats a material containing 25-40 per cent of sulfur should produce an iron with a sulfur content as low as 0.001 per cent and consistently 0.004 per cent.

THE FUTURE OF ELECTROLYTIC IRON.

In the preceding pages the development of electrolytic iron has been hastily traced. It has been shown that with the exception of two highly specialized uses in small tonnages the only process today that produces electrolytic iron in a commercial way is the Grenoble plant. The progress of the Milford Electrolytic Iron Company in attempting to produce finished tubes and sheets directly from the ore has been traced. This process is not technically and commercially complete as yet.

The vital question arises immediately: what are the advantages of electrolytic iron?

A great many claims that have been advanced must be modified or abandoned completely until new evidence is brought forth to support them.

Much has been said of the magnetic properties of electrolytic iron, but Yensen[30] and others have shown clearly that the only electrolytic iron which has any extraordinary properties is that which has been melted *in vacuo*. It will be generally admitted that large tonnages of electrolytic iron melted *in vacuo* on a competitive basis with present magnetic materials cannot be considered as commercial, at least not yet.

The non-corrodible character of electrolytic iron is often spoken of. However all electrolytic iron does rust, and more readily than is commonly imagined. In fairness it should be said that electrolytic iron is in general less attacked than ordinary iron and steel, but where resistance to corrosion is the important factor the engineer will go to copper, zinc, lead, chrome iron, etc.

As a base material for alloys electrolytic iron demands attention because of its purity. The following table shows roughly a comparison of various irons.

	Swedish Iron Per cent	Grenoble Iron Per cent	Milford Iron Per cent
C	0.160	0.029	0.030
Si	0.050	0.004	0.002
S	0.007	0.005	0.003
P	0.034	0.004	0.002
Mn	0.013	nil	nil

The writer feels confident that, as the Milford process develops, the percentage of metalloids (especially carbon, which comes from the wooden tanks) will fall considerably, to be replaced by small amounts of zinc and lead.

The important consideration is price, and it seems doubtful whether crude electrolytic iron can compete with the present forms of commercially pure iron.

Another interesting property of electrolytic iron is its ducility, when made in the form of sheets and tubes. Although some recent tests made on French iron in this country have indicated no advantage in this respect for electrolytic iron, it must be admitted that electrolytic iron properly made and heat-treated is more ductile than mild steel. The commercial uses of the Grenoble iron, and practical rolling tests in this country, are a strong indication of this. If, then, a highly ductile iron can be made in thin

[30] Yensen, Electrician, **75**, 119 (1915); Proc. Am. Inst. Elec. Eng., **34**, 237-62 (1915); Univ. Ill. Eng. Exp. Sta., Bull. **77** (1915).

gauges at a competing price with cold-rolled strip a tremendous field is opened up. There may also be a use for such ductile iron in wire-drawing. The tube field seems to be the most promising for electrolytic iron. For example, charcoal iron boiler tubes cannot be made seamless and it would appear that thin, uniform tubes of very pure electrolytic iron could be introduced. Tests have shown that electrolytic iron properly treated has the necessary mechanical strength.

There are cases where it would seem practicable to leach high copper-bearing ores, recovering the copper by cementation. In such cases the iron produced would be the secondary product, and the economic aspect of electrolytic iron would be changed.

DISCUSSION.

T. B. HINE[31]: I notice that in the process Mr. Belcher described, as well as in the French process, a chloride solution is used. Is it because experiment has shown that the sulfate will not permit the deposition of the coherent tubes required? Of course, I understand that for the Milford process a chloride must be used, but I am wondering whether iron, in the form of thin tubes, can be deposited from a sulfate solution.

ALFRED STANSFIELD[32]: I have listened to Mr. Belcher's paper with great interest, as some of my own students have made studies of the Milford process in the laboratory. The process has been tested on a considerable scale at Trail, British Columbia, and a further investigation is being undertaken in the laboratories of the Department of Mines, Ottawa.

T. B. HINE: There might be a number of possibilities in the manufacture of electrolytic iron if one could use the sulfate to produce thin tubes that were coherent. For instance, mention has been made several times here of copper sulfate being rather a drug on the market. If copper sulfate is available it might be cemented out with iron, and the iron sulfate electrolyte might be used to produce iron; or where copper is leached from ores

[31] Research Chemist, Western Electric Co., Hinsdale, Ill.
[32] Prof. of Metallurgy, McGill Univ., Montreal, Canada.

it could be cemented out with scrap iron. If electric power were available it might be utilized to make a special thin iron that could satisfy certain commercial needs. The advantage as to cost would be in getting thin iron sheets instead of thick iron sheets, which are at present made cheaper by rolling down from a cast ingot.

WILL BAUGHMAN[33] (*Communicated*): A great deal of research work has been done on the subject of electrolytic iron, and practically all technical features have been thoroughly investigated. The conditions that now prevent the establishment of large plants for the manufacture of electrolytic iron are not of a technical nature, but more of an economic character. Thirty-five years ago copper tubes of a superior quality were manufactured, electrolytically, at several European plants. Some of these plants or their successors are in operation at present with production capacities of ten to twenty tons of tubes and similar material per day.[34] Both partially and completely submerged rotating mandrel cathodes and various types of burnishers were used. The anodes, which were on the floors of the cells, were either bars or copper granules and shot. There were no diaphragms.

Here on the Pacific Coast we have some large deposits of high-grade iron ore, but no coking coal. Various attempts have been made in the past to utilize these ores by using either one or more of the following cheap and plentiful materials: crude oil, natural gas, lignite coal or hydro-electric power.

Electric smelting, using charcoal as a reducing agent, was tried on a large experimental scale at Heroult, Cal. At eight different points on the Pacific Coast, reduction or metallizing of the ore to sponge iron was tried on a semi-commercial scale. One plant used rolls to compact large bars of white hot sponge into billets.[35]

The trouble has been that such products contained little or no manganese, silicon or carbon, and consequently had a high melting point. In fact, they were compelled to compete with scrap steel for a market.

Ten years ago it occurred to me that sponge iron might be used as an anode for electrolytic refining. Sponge iron at that

[33] Consulting Metallurgist, Los Angeles, Calif.
[34] Electro-Metallurgy by John B. C. Kershaw, pp. 124-134.
[35] The Electric Furnace for Iron and Steel by Alfred Stansfield, pp. 141-173, for partial information.

time was being widely investigated for use as a precipitant of copper in the hydrometallurgy of copper ores.[36]

No real difficulties were encountered in the usual laboratory tests, using a cell about 4 x 4 x 8 in. long (10 x 10 x 20 cm.). Kern's electrolyte[37] proved the cheapest and most reliable of some two dozen that were investigated. Some of the iron ore was not completely reduced to sponge metal, but the resultant FeO helped form the oxychloride that is considered an essential feature at Grenoble. The sponge iron itself is an efficient depolarizer.[38]

TABLE I.

Cost and Recovery of Electrolytic Iron.

Operation	Magnetite Ore	Titaniferous Ore
Mining	$1.00	$1.00
Transportation	2.50	1.50
Crush and Briquette, etc.	1.25	1.25
Metallizing and annealing	1.00	1.25
2 bbl. crude oil	2.50	2.50
Refining, Ti and V	...	4.25
Electric power, 1200 kw. hr.	9.60	9.60
Repairs, depreciation, amortization, interest, insurance, taxes	6.00	6.00
Labor, etc., 55 men	3.50	4.00
Sales expense, etc.	6.50	9.50
	$33.85	$40.85
Products		
1,000 lb. tubes, etc., @ 5 cents	$50.00	$50.00
300 lb. TiO_2 @ 8 cents		24.00
15 lb. V_2O_5 @ $1.00		15.00
	$50.00	$89.00

Larger scale experiments were then made to obtain data on probable costs, and in spite of the fact that less electric power per ton was used than for electric smelting at Heroult, and incidentally only half that indicated by Mr. Belcher for the Milford process, we found that there were many economic problems to be solved.

My next step was to experiment with the titaniferous iron ores located on the outskirts of Los Angeles. These ores contain 50 to 65 per cent Fe, 14 to 22 per cent TiO_2 and 0.50 to 1.27 per cent V_2O_3. Crude oil was used as a reducing agent. Considerable

[36] Trans. Am. Inst. Mining & Metall. Eng., 49, 648-654, 694-700.
[37] Trans. Am. Electrochem. Soc., 13, 103 (1908).
[38] Cowper-Coles, U. S. Patent 1,127,966.

difficulty was encountered in metallizing the sponge at first, and additional treatment was necessary. On the other hand, with only little extra cost titanium oxide 98 per cent pure was produced and up to 80 per cent of the vanadium recovered. Probable costs and recoveries, per ton ore on 100-ton per day scale, are recorded in Table I.

This would indicate commercial possibilities where a valuable by-product can be recovered. Experiments on certain eastern ores, that contained nickel, indicate that this element might be recovered in a measure with the titanium and vanadium. With slight change in treatment, chrome iron ores also can be treated, and a good grade of chrome oxide pigment produced.

It is my opinion that the commercial success of the Milford process will depend solely upon the value of the by-products, which will, of course, vary with the individual ore. In my method herein described the costs per ton should be less than the Milford costs. Mining, transportation and fine crushing are required in both. The metallizing costs are offset by leaching and filtering costs. The electrolysis of sponge iron will cost less, as no diaphragms are needed and a much lower voltage is used. The recovery of sulfur, copper, nickel and other metals will cost as much, if not more than the costs of recovering the titanium and vanadium oxides.

I have been privately informed that electrolytic iron on a thirty-ton per day scale was produced in Germany during the war. This iron was used to make wire for electrical transmission of power. I might also cite references to a Swiss plant, a German plant and a plant at Firminy, France.[39]

DONALD BELCHER (*Communicated*): The use of sponge iron as anode material for the manufacture of electrolytic iron has been suggested at various times, but I, personally, have never tried it. I heartily agree with Mr. Baughman that the cost of leaching and filtering would more than offset the metallizing costs, and it would be a great relief to get rid of the extremely corrosive ferric chloride. Also, given perfect anodic conditions, the voltage of the sponge iron cell would be much lower than that of the Milford cell, and there would be no diaphragm to contend with.

[39] J. four Electrique et Electrol., **27**, 89 (1918); Elektrotechn. Zeitsch. **42**, 138 (1921); Echo des Mines-Lumière élect., **35**, 241.

But I would think that the physical character of sponge iron would make it difficult to establish and maintain good electrical connections in the cell. Also it might be difficult to pack a sufficient amount of sponge iron in a cell so that too frequent chargings would not have to be made.

Mr. Baughman indicates that the non-metallic impurities in iron made this way should be very low, but he tells us nothing of metallic impurities which might deposit with the iron. I am in perfect agreement with the idea that successful production of electrolytic iron from ores will depend upon the value of the by-products.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, Mr. S. Skowronski in the Chair.

THE ELECTROLYTIC PRODUCTION OF BERYLLIUM.[1]

By B. S. Hopkins[2] and A. W. Meyer.[2]

Abstract.

Residues from Texan gadolinite were treated with HCl and $NaHCO_3$, to separate iron and aluminum from beryllium. Beryllium basic carbonate was prepared, from which a double fluoride, essentially $NaBeF_3$, was obtained. This salt was fused and electrolyzed, using a carbon anode, a nickel crucible as cathode, and a current of 6 amp. at 110 v. Metallic beryllium was obtained as thin flakes scattered through the electrolyte, and mixed with beryllium oxide and carbide. The metal was separated from everything except the oxide by sprinkling into water; the oxide was removed by centrifugal force. Metal of 98 per cent. purity was obtained, but the yields were poor.

The electrolysis of fused beryllium halides presents unusual difficulties. The inability of the simple salts to carry the electric current is easily remedied by adding to the melt some halide of an alkali metal. When metallic beryllium has been deposited on the cathode, it shows a decided tendency to alloy or form a compound with the material of the cathode, and to unite with the oxygen of the air. If these reactions are prevented, beryllium forms a thin coating on the cathode, but it does not collect as a compact metal.[3] Small, thin flakes peel off, and are distributed by convection currents through the molten electrolyte.

[1] Manuscript received February 9, 1924.

[2] Contribution from the Chemical Laboratory of the University of Illinois, Urbana, Ill.

[3] Stack and Goldschmidt, U. S. Patent, 1,427,919, September 5, 1922, claim to obtain compact beryllium by electrolysis of a bath of fused sodium beryllium fluorides.

The material used in this investigation was obtained from Texas gadolinite, which is estimated to contain 11.33 per cent BeO. The ore was finely ground, extracted with an excess of HCl, to which a little HNO_3 was added at intervals. Silica was removed by dehydration, and the rare earth salts precipitated with hot saturated oxalic acid solution. The filtrate from this operation contained the beryllium, together with a large amount of iron and smaller amounts of calcium, aluminum, sodium and other metals.

This solution was neutralized with ammonia, and then an excess of NaOH was added, precipitating the beryllium and iron hydroxides together. The precipitate was removed, washed and stirred with enough HCl to dissolve about two-thirds of the whole mass. This treatment brought practically all the beryllium into solution, and left undissolved a large part of the iron hydroxide. The acid extract was filtered, heated to boiling, and concentrated NaOH solution was added cautiously, until a small amount of freshly filtered liquid gave a light colored precipitate with ammonium hydroxide, showing that nearly all the iron had been precipitated.

This material was again filtered, and the filtrate was evaporated to the saturation point, and then stirred into a boiling concentrated solution of sodium bicarbonate. After cooling, the clear liquid was decanted, and the extraction with sodium bicarbonate repeated. The combined filtrates were acidified with HCl, heated to boiling, and basic beryllium carbonate precipitated by adding a saturated solution of sodium carbonate. After boiling thoroughly, the basic carbonate was filtered off, washed and dried at 100° C.

The basic beryllium carbonate prepared in this manner was pure white in color, and completely soluble in sodium bicarbonate solution. Hence it was free from both iron and aluminum. It contained a small amount of sodium carbonate as an impurity, but this was not objectionable, since later treatment converted the sodium carbonate into the fluoride, which was necessary for the electrolysis. Upon analysis the basic beryllium carbonate was found to contain 26.1 per cent BeO.

In order to obtain a melt which conducts the electric current reasonably well, we used a mixture of sodium fluoride and beryllium fluoride. It has been shown that beryllium fluoride is soluble in all proportions in fused sodium fluoride, and that there are two definite double fluorides of the formulæ $NaBeF_3$ and Na_2BeF_4 respectively. It is therefore possible to mix the fluorides of sodium and beryllium in various proportions. Since the melting point of beryllium fluoride is 800° C., and of sodium fluoride is 980° C., an increase in the proportion of beryllium in the mixture lowers the fusion point. This is a decided advantage, not only because of the greater ease with which the electrolysis is carried out, but, more important still, the lower temperature minimizes the tendency of the metallic beryllium to oxidize.

Another advantage of a large proportion of beryllium fluoride in the electrolyte is to be noted in connection with the separation of the metallic beryllium from the melt. This is accomplished by dissolving the electrolyte in water. Since beryllium fluoride is much more readily soluble than sodium fluoride, as the per cent of the former increases the solubility of the mixture becomes greater, and the separation of the metal is facilitated. On the other hand, if too large a proportion of beryllium fluoride is used in the electrolyte the resistance to the electric current is greatly increased, and higher voltages become necessary. If too high voltages are used the current produces overheating, with increased oxidation of the metal and increased tendency to alloy with the cathode material. After considerable study it was decided to use an electrolyte corresponding closely to the composition $NaBeF_3$.

In the preparation of the desired double salt 125 g. of 48 per cent hydrofluoric acid were weighed out in a platinum evaporating dish, and 53 g. of pure sodium carbonate were added in small portions. Then the solution was diluted with 50 cc. of distilled water and neutralized with the prepared basic beryllium carbonate. The resulting solution was evaporated to dryness over a low flame, and the residue thoroughly fused. After cooling, the salt was broken up into small pieces and used in the electrolysis. Pre-

pared in this manner, the double fluoride was transparent, easily fusible, completely soluble in water, and approximately of the composition indicated by the formula $NaBeF_3$.

The electrolysis was carried out in a nickel crucible of about 200 cc. capacity, which served as the cathode. The anode was a carbon rod which was lowered into the electrolyte until it was about 1 cm. from the bottom of the crucible. The crucible was fitted into a round opening in a heavy asbestos board, which

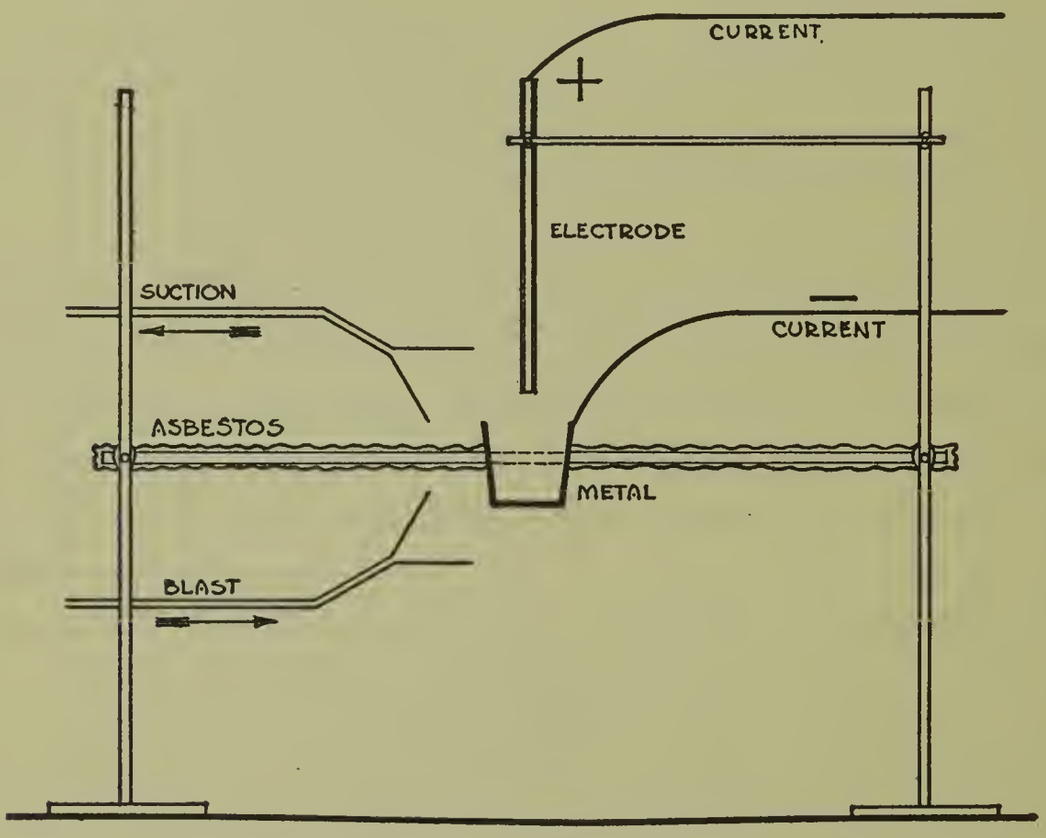

FIG. 1. Apparatus for the Production of Beryllium.

served the double purpose of insulator and protection from the gases of the burner used in the fusion of the electrolyte. Gases liberated by the electrolysis were removed by means of a bent glass funnel, which was connected with the exhaust. The current used was from a 110-volt generator, and was kept constant at 6 amp. during the runs.

Each run was started by fusing the electrolyte with a four-way burner placed under the crucible. As soon as the sodium beryllium fluoride had melted the carbon anode was lowered into

place and the current started. The resistance to the passage of current was sufficient to maintain the temperature of fusion, consequently the burner was removed and a blast of cold air driven over the bottom of the crucible. This served to chill the outer layer of material, and was effective in preventing the beryllium from alloying with the nickel crucible. The electrolysis was continued until the ammeter showed that no more current was passing.

Considerable difficulty was experienced in finding the proper size of carbon anode. At first rods of about 0.5 cm. diameter were used, but the anode effect with these was so troublesome that little beryllium was obtained. Rods 2.5 cm. in diameter removed the trouble from the anode effect, but these large rods increased the amount of beryllium carbide so much that little metallic beryllium was left. It was finally determined that a rod of 1 cm. diameter was most efficient for our form of apparatus. With such a rod the anode effect was slight, and only a little beryllium carbide was formed.

During the progress of the electrolysis, as the beryllium was removed, the melting point of the electrolyte increased and its conductivity decreased. As a result freezing of the bath and interruption of the current resulted. These circumstances were easily prevented by adding to the crucible small amounts of fresh $NaBeF_3$. Beryllium oxide dissolved readily in the fused electrolyte, and its addition permitted the run to be prolonged materially. It was found, however, that such additions did not increase the yield of beryllium metal, since the best yields were obtained by shutting off the current as soon as the ammeter indicated a marked increase in the resistance of the electrolyte.

After the completion of a run it was found to be helpful to dip the lower part of the hot crucible into cold water. This treatment left the electrolyte in the form of a fine gray powder, which was easily removed from the crucible. This powder was composed of sodium fluoride, beryllium fluoride, beryllium carbide, beryllium oxide, and small flakes of metallic beryllium. When this powder was sprinkled in small amounts into a large volume of water, the fluorides of sodium and beryllium dissolved, and

the carbide decomposed, while the metallic beryllium and its oxide were unchanged. Since the metal is somewhat soluble in both acid and alkaline solutions, it was desirable to keep the solution as nearly neutral as possible. Accordingly, the powdered mixture was added to a large volume of water, and at intervals a little dilute HCl was added to correct the alkalinity which developed in the solution. The acid which was added also prevented the precipitation of beryllium hydroxide when beryllium carbide was decomposed.

After this process had been completed, a mixture of beryllium and beryllium oxide settled to the bottom of the jar. This was filtered, thoroughly washed and dried. The separation of the oxide from the metal was accomplished by means of centrifugal force. The metal has a density of 1.85 and the oxide of 3.01.

Accordingly, the dry powder was whirled in a mixture of ethylene bromide and alcohol, whose density was about 1.9. By repeating this operation several times the oxide was almost wholly removed. The resulting metal was found to be 98 per cent pure, but the yields were very poor. In some runs no appreciable amount of beryllium was obtained, and the best yield scarcely exceeded 13 per cent of the beryllium used.

SUMMARY.

Beryllium was extracted from Texas gadolinite, and separated from iron and aluminum by the partial solubility of the hydroxides in HCl, and the total insolubility of ferric hydroxide in sodium bicarbonate solution.

Pure $NaBeF_3$ was prepared by dissolving in HF the calculated amounts of sodium carbonate and basic beryllium carbonate.

Fused sodium beryllium fluoride was electrolyzed in a nickel crucible, using a carbon anode and a current of 6 amp. at 110 v.

Metallic beryllium was obtained as small thin flakes, mixed with the electrolyte and varying amounts of the oxide and carbide of beryllium. The metal was separated from all of these materials except the oxide by sprinkling into water; the oxide was removed by centrifugal force.

Metallic beryllium of 98 per cent purity was prepared, but the best yields scarcely exceeded 13 per cent of the beryllium used.

DISCUSSION.

H. S. Cooper (*Communicated*)[4]: In my opinion, any fluoride disclosed either by the writers of this paper or by others is not satisfactory for making even experimental quantities of beryllium as long as the bath is maintained at a temperature which influences the separation of the metal in the form of powder, or flaky crystals. Great difficulty is experienced in the separation of the metal in these forms from any fluoride mass, and, as pointed out by the authors, only a low yield of metal is obtained.

Recently, I have had occasion to prepare several hundred grams of metallic beryllium, and by special treatment a purity of 98 per cent was easily obtained. The metal is initially produced in the form of large, bright crystals, but can be converted readily into fused buttons or ingots. For various reasons the method of manufacture cannot be discussed at this time, but it is hoped that the details of this process may be published at a later date. The method is satisfactory for making sufficient amounts of beryllium for experimental purposes, and, with some modification, fair-sized quantities could probably be produced.

MAGNESIUM AND THE OXIDE PROCESS.

W. G. Harvey[5]: Magnesium can be electrolyzed from either the chloride or the oxide. With the chloride, the operating temperature is lower, since a double salt of either sodium-magnesium or potassium-magnesium chloride can be used. The most expensive part of the operation is the dehydration of the magnesium chloride to the fused state, for it tends to decompose very easily, unless special precautions are taken, forming the insoluble magnesium-oxychloride. Metal produced from this electrolysis is likely to contain the hygroscopic chloride, unless extreme care is taken in its elimination.

The oxide process uses an electrolyte of fused fluorides, in which magnesium oxide is suspended. The operating temperature is

[4] Kemet Laboratories Company, Inc., Cleveland, Ohio.
[5] Vice-President, American Magnesium Corporation.

about 900° C. If a good grade of oxide is purchased no purification of it is necessary. Carbon electrodes are used, and they are consumed in exact proportion to the magnesium produced. The process is continuous, the molten magnesium metal being removed from the cathode compartment at intervals.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, Mr. S. Skowronski in the Chair.

THE METALLURGY AND ALLOYS OF BERYLLIUM.[1]

By E. A. Engle[2] with B. S. Hopkins.[3]

Abstract.

A critical study of the electrometallurgy of beryllium establishes the fact that beryllium oxide is soluble in various fused salts, from which solutions metallic beryllium may be deposited electrolytically. More efficient results are secured by the electrolysis of a fused bath of barium fluoride and sodium beryllium fluoride. These electrolytes combine such desired properties as density, relative inertness and suitable melting temperature. The use of a molten metal cathode yields directly the corresponding beryllium alloy in many cases.

The general methods applied in the metallurgy of beryllium have been the reduction of the oxide or anhydrous halides, or the electrolysis of its fused salts. The reduction of the oxide by means of potassium, magnesium, carbon, aluminum and calcium respectively, has been studied, but no reported results indicate the possibility of its technical preparation by these methods. The reduction of the anhydrous halides by sodium or potassium was the original method of the preparation of beryllium. Wöhler[4], Bussy[5], Debray[6], Reynolds[7], Nilson and Pettersson[8], Humpidge[9],

[1] The investigation was carried out under the fellowship established by the E. I. duPont de Nemours and Company, to whom we express our obligation. Manuscript received January 21, 1924.

[2] This report is an abstract from a portion of a thesis submitted by E. A. Engle, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, at the University of Illinois.

[3] Dept. of Chemistry, University of Illinois, Urbana, Ill.

[4] Wöhler, F., Ann. chem. phys., (2) **39**, 77 (1828).

[5] Bussy, Berzelius Jab., **9**, 97 (1828).

[6] Debray, H., Chem. Zentr., **26**, 549 (1855); Bull. Soc. chem., **7**, 465 (1867).

[7] Reynolds, J. E., Chem. News, **35**, 119 (1877).

[8] Nilson, L. F., and Pettersson, O., Chem. Z. [Series 3, **9**,] **49**, 275, (1878).

[9] Humpidge, T. S., Chem. News, **47**, 181 (1883).

Kruss and Moraht[10], and finally Hunter[11], have reported further investigations of this method. None of these investigators used finely divided sodium. The following reductions were made using sodium which had been finely granulated under xylene and anhydrous sodium beryllium fluoride. The results show this is the most direct method of preparing beryllium in powder form.

1. Ten grams of powdered anhydrous $NaBeF_3$ were mixed with 10 g. of sodium. The sodium had been previously granulated under xylene to the size of fine sand, washed with anhydrous ether, leaving a trace of residual ether to prevent oxidation. Twice the theoretical quantity of sodium was used. The mixture was placed in an iron boat and heated in an iron tube to 800° at 10 mm. pressure for 30 min., then cooled under the same pressure. Under these conditions the excess sodium distilled off. The product, a gray sintered mass, was slightly reactive towards water, and gave a marked liberation of hydrogen when treated with dilute HCl. This gray mass was treated with large volumes of 2 per cent $HC_2H_3O_2$ to remove any excess sodium, washed for 48 hr. with faintly acidulated water, and thoroughly dried. The material showed on analysis beryllium, iron, and some $Be(OH)_2$. It had a density slightly greater than 2.0.

2. In this run conditions were modified so as to reduce surface oxidation. A heating tube was prepared from malleable iron pipe, capped at the lower end, water cooled at the upper. It was fitted with stopper and stopcock. A sheet iron crucible was used to contain the charge. Twenty grams of powdered $NaBeF_3$ was thoroughly mixed with 20 g. of granulated sodium, covered with a layer of NaF, and placed in the heating bomb. After heating for 45 min. at 850° and 7 mm. pressure, a clinker of gray material remained in the crucible. This was purified as above, and proved to be powder beryllium, containing some iron, BeO and unreduced fluorides.

ELECTROLYSIS OF FUSED SALTS.

The most generally satisfactory methods for the production of beryllium have been electrolytic. Important investigations have

[10] Kruss and Moraht, Ann. der Chem., **260**, 161 (1890).

[11] Hunter, M. A., Orig. Commun., Eighth Inter. Cong. of Applied Chem. Inorg., **2**, 125 (1912).

been made by Becquerel[12], Humpidge[13], Graetzel von Graetz[14], Warren[15], Borchers[16], Liebmann[17], Lebeau[18], Oesterheld[19], Copaux[20] and Meyer.[21] Due to its high melting point (1278°) and low density (1.61 to 1.85), its preparation by electrolysis presents difficulties not encountered in the metallurgy of other metals, and it is doubtful if pure beryllium has ever been directly prepared in the massive form. When the metal is produced by the electrolysis of fused salts, small non-coherent flakes are deposited in the cathode.[22] These scale off, remain suspended in the bath due to their density, become disseminated through the melt by convection currents and are easily oxidized. The collection, purification and fusion of these flakes is difficult and tedious.

In the experimental work outlined below, suitable electrolyte formulæ and apparatus have been developed to yield a purer and more available product. Simultaneously, experiments with molten metal cathodes have developed apparatus and formulæ for the direct preparation of the beryllium-aluminum alloy, and more satisfactory methods for the preparation of several of the beryllium alloys. The work is exploratory in character. Many conditions, new and varied electrolytes and materials, have been investigated to determine the most favorable circumstances for the direct preparation of beryllium and its alloys. Lebeau[23], Ivinson[24] and Oesterheld[25] report related investigations of the alloys of beryllium.

The electrolyses tabulated in the table on the following pages were all carried out with an average charge of 100 g. The material was always in a thoroughly molten and fluid state. The more important details only are listed.

[12] Becquerel, A. C., Ann. Chim. phys., 48, 350 (1831).
[13] Humpidge, T. S., Chem. News, 47, 181 (1883).
[14] Graetzel von Graetz, A., Chem. Ind., 14, 499 (1891).
[15] Warren, H. N., Chem. News, 72, 310 (1895).
[16] Borchers, W. J., Chem. Soc. (London), 70, 521 (1896).
[17] Liebmann, L., Chem. Ztg., 23, 525, 944 (1899).
[18] Lebeau, P., Chem. Zentr., 11, 69, 750 (1898).
[19] Oesterheld, G., Z. anorg. Chem., 97, 1 (1916).
[20] Copaux, H., Comptes. rend., 171, 630 (1919).
[21] Meyer, A. W., Unpublished Thesis, University of Illinois, (1918).
[22] Stack and Goldschmidt, U. S. Patent 1,427,919, September 5, 1922, claim to obtain compact beryllium by electrolysis of a bath of fused sodium beryllium fluorides.
[23] Lebeau, P., Chem. Zentr., II, 69, 750 (1898).
[24] Ivinson, C. H., Metal Ind., 11, 340 (1913).
[25] Oesterheld, G., Z. anorg. Chem., 97, 1 (1916).

Runs 1-10. Preliminary experiments established the solubility of BeO in fused cryolite, and the electrical conductivity of the resulting solution.[26] Electrolysis of such fused solution yielded small amounts of flake Be, and when electrolyzed to molten metal cathodes yielded low Be alloys of Al, Sn, Ag, etc. Simultaneous electrolysis of Al_2O_3 and BeO in fused cryolite yielded only Al. The high temperatures necessary, and consequent oxidation and carbide formation is a serious difficulty. The fact that the density of the metal formed is nearly the same as that of the fused electrolyte results in dissemination and mixing. The materials are easily obtainable, and there is no difficulty in dehydration. Electrode graphite is the most suitable material for the apparatus.

Runs 11-12. A solution of BeO in anhydrous $CaCl_2$ fused at a low temperature (650°) and yielded on electrolysis pellets of a Ca-Be alloy and flakes of Be metal. On prolonged heating the charge became too viscous, due to volatilization and increasing basicity.

Runs 13-15. Electrolysis of BeO in fused NaCl + KCl gave flake Be contaminated with Na. The non-corrosive character of the charge is advantageous in that containers and apparatus may be of iron.

Runs 16-25. Electrolysis of BeO in fused $NaBeF_3$ yielded flake Be. Attempts to form the Al alloy directly were at first unsatisfactory, since the Be floats on the bath and is oxidized. An inverted cup cathode chamber was next developed. It served efficiently in the collection of the flake Be and the prevention of its dissemination. Molten Al being heavier than the bath, however, failed to remain in the bell to alloy (as molten metal cathode). Tungsten was proved a satisfactory electrode material, being much superior to Ni, Pt, Fe or C, which alloy with Be. Pyrex glass was suitable container material.

Run 26. The addition of fused cryolite yielded a mixture which separated into layers on standing, and was too viscous for electrolysis.

Runs 27-33. A mixture of BaF_2 (60 per cent) and $NaBeF_3$ (40 per cent) was developed having a satisfactorily low melting

[26] Solutions of BeO in fused salts were described by Cooper, U. S. Pat. 1,254,987; C. A., 12, 674 (1918).

TABLE I.

Electrolytic Production of Beryllium Alloys.

Charge 10 per cent BeO in fused cryolite, 950°

Run	Anode	Cathode	Container (Crucible)	Current Voltage	Yield
1	Nichrome Wire No. 8	Graphite Crucible	Graphite	7.5 amp. 3 v.	Ni flakes, trace Be (1)
2	Carbon rod, 1.3 cm.	Molten Al	Graphite	10 amp. 8 v.	Al pellets, trace Be (2)
3	Carbon rod, 1.3 cm.	Molten Al	Graphite	8 amp. 8 v.	Al ingot, trace Be (3)
4	Carbon rod, 1.3 cm.	Molten Pb	Duriron	4.5 amp. 5.4 v.	Pb buttons, no Be
5	Carbon rod, 1.3 cm.	Molten Sn	Duriron	5 amp. 5.4 v.	Sn film with much Be
6	Carbon rod, 1.3 cm.	Molten Ag	Duriron	4.2 amp. 5.4 v.	Ag-Fe button (4)
7	Carbon rod, 1.3 cm.	Molten Ag	Graphite	5 amp. 5 v.	Ag button, with trace Be
	Charge 7 per cent Al_2O_3 in fused cryolite 1000°				
8	Carbon rod, 1.3 cm.	Graphite Crucible	Graphite	8 amp. 4-8 v.	Al pellets (5)
	Charge 10 per cent Al_2O_3, 10 per cent BeO, 80 per cent cryolite fused 950°				
9	Carbon rod, 1.3 cm.	Graphite Crucible	Graphite	6 amp. 4 v.	Al pellets, trace Be
	Charge 15 per cent BeO, 8 per cent Al_2O_3, 77 per cent cryolite, fused 950°				
10	Carbon rod, 1.3 cm.	Graphite Crucible	Graphite	5 amp. 7 v.	0.5 g Al 0.2 per cent Be
	Charge 5 per cent BeO in fused $CaCl_2$ 650°				
11	Nichrome Wire No. 8	Nichrome Wire No. 8	Porcelain	10 amp. 20 v.	Vitreous mass (6)
12	Nickel Crucible	Sheet iron bell	Nickel	10 amp. 5 v.	Ca-Be Pellets (7)

1. Crucible disintegrated.
2. Molten Al came to top.
3. Much carbide.
4. Crucible melted.
5. Check apparatus.
6. Crucible corroded.
7. Charge became viscous.

Table I—Continued.

Charge 10 per cent BeO, 45 per cent NaCl, 45 per cent KCl 900°

Run	Anode	Cathode	Container (Crucible)	Current Voltage	Yield
13	Carbon rod, 2 cm.	Sheet iron Crucible	Sheet iron	12 amp 17 v.	Pellets Na Flake Be
14	Carbon rod, 1.3 cm.	Molten Al	Graphite	20 amp. 3 v.	Al button trace Be (8)
15	Carbon rod, 1.3 cm.	Molten Al	Graphite	8 amp. 8 v.	Al button surrounded by shell of powder BeO
	Charge 10 per cent BeO in fused $NaBeF_3$ 625°				
16	Carbon rod, 1.3 cm.	Molten Al	Graphite	1.5 amp. 6 v.	Al ingot trace Be (9)
17	Carbon rod, 1.3 cm.	Molten Al	Pyrex Beaker	2 amp. 6 v.	Al button floated breaking circuit
18	Carbon rod, 1.3 cm.	Pt wire in glass chamber	Pyrex Beaker	2 amp. 10 v.	Na-Be alloy Pt-Na-Be Much BeO
19	Duriron Crucible	Ni sheet in glass chamber	Duriron	5 amp. 6 v.	BeO and flake Be
20	Duriron Crucible	W rod 1 cm. sq.	Duriron	5 amp. 6 v.	Gray powder Be
21	Carbon rod, 1.3 cm.	Molten Al	Duriron	5 amp. 8 v.	Al buttons + 2% Be
22	Tungsten Rod	Molten Al	Duriron	5 amp. 6 v.	Al dispersed through melt flake Be
23	Carbon rod, 1.3 cm.	Molten Al in glass chamber	Pyrex Beaker	5 amp. 10 v.	Pellets pure Al Flake Be-BeO
24	Carbon rod, 1.3 cm.	Molten Al in glass chamber	Pyrex Beaker	5 amp. 6 v.	Al and Be (10)
25	Duriron Crucible	Mg in glass chamber	Duriron	5 amp. 8 v.	MgO
	Charge BeO 8 per cent, cryolite 46 per cent, NaBeF 46 per cent, fused 800-900°				
26	Carbon rod, 1.3 cm.	Molten Al	Graphite	4 amp. 10 v.	Al dissem. Flake Be (11)

8. Molten Al floated.
9. S and C from crux.
10. Disseminated.
11. Charge liquated.

TABLE I—Continued.

Charge $NaBeF_3$ 60 per cent, BaF_2 40 per cent, fused 850°

Run	Anode	Cathode	Container (Crucible)	Current Voltage	Yield
27	Graphite Crucible	Al in iron chamber	Graphite	4.7 amp. 2.5-3 v.	Al-Fe-C-Be + BeO (12)
28	Graphite Crucible	Al in graphite Crucible	Graphite	5 amp. 3-10 v.	Carbide of Be and Al
29	Graphite Crucible	Al in iron chamber	Graphite	4.5 amp. 5 v.	Pellets Al Flake Be + BeO (13)
30	Graphite Crucible	Al in sheet iron chamber	Graphite	.. ..	(14)
31	Graphite Crucible	Al in iron chamber	Graphite	5 amp. 6-10 v.	Al-Be alloy + Fe + C
32	Graphite Crucible	Inverted iron crux	Graphite	10 amp. 7-8 v.	BeO + Na Na — Be
33	Graphite Crucible	Inverted iron crux	Graphite	10 amp. 7 v.	BeO + Flake Be
		Charge NaCl, $BaCl_2$, BeO			
34	Iron Crucible	Iron bell	Iron	10-15 amp. 5 v.	(15)
		Charge Beryl in $CaCl_2$ fused 800°			
35	Carbon rod, 1.3 cm.	Graphite Crucible	Graphite	7 amp. 8 v.	Be formed and burned as rapidly
		Charge Beryl in Na_2SiF_6 fused 900°			
36	Carbon rod, 1.3 cm.	Molten Al	Graphite	10-50 amp. 16 v.	Al-Si alloy + BeO
		Charge Crude Na_2BeF_4 as extracted, 700°			
37	Carbon rod, 1.3 cm.	Nickel Crucible	Nickel	10 amp. 84 v.	Be + BeO + Na + carbide

12. Non-homogeneous metal.
13. Entrapped air.
14. Cathode chamber corroded.
15. Marked volatilization.

point (750°) and high density (3.476), and containing no easily reducible metal salt other than Be. Electrolysis of this fused bath to a molten Al cathode gave good yields of Al-Be alloy.

The best cathode chamber is an inverted cast iron cup, tinned on the inside to insure electrical contact with the Al, and filled so as to avoid entrapped air. This furnishes a most satisfactory and direct method for the preparation of this alloy. Electrolysis to the iron bell without the molten Al yielded impure Be.

Run 34. The substitution of the chlorides for the more corrosive fluorides proved unsuccessful.

Runs 35-36. The direct electrolysis of the ore beryl in a molten flux of $CaCl_2$ of Na_2SiF_6 was not promising.

Run 37. The electrolysis of the crude Na_2BeF_4 directly, as prepared in the extraction of beryl with Na_2SiF_6, gave a good yield of flake Be and obviated many steps in the conversion and purification of the salt.

SUMMARY.

The reduction of sodium beryllium fluoride with granulated sodium was investigated, and furnished the most direct method of preparing beryllium in powder form.

The solubility of beryllium oxide in various fused salts was established; the conductivity of the resulting solutions was studied, and their efficiency in the preparation of beryllium metal determined.

Electrolytes, apparatus and materials were developed for the preparation of flake beryllium in a relatively pure form and lessened dissemination.

The beryllium-aluminum alloy was directly prepared, and efficient conditions for its preparation were established. The alloys of beryllium with silver, tin, calcium and nickel were prepared in similar manner.

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DISCUSSION.

H. S. Cooper (*Communicated*)[27]: I am glad to note that this subject is receiving some of the attention which it unquestionably

[27] Kemet Laboratories Co., Inc., Cleveland, Ohio. Mr. Cooper was represented by Mr. M. D. Sarbey who exhibited at the meeting a large number of interesting beryllium alloys and products.

merits. The authors are attacking the problem from the right angle, and their efforts to find the best solvent for beryllium oxide, as well as to make aluminum-beryllium alloys in an efficient manner, deserve commendation. These alloys are of special interest to me; a patent covering the Al-Be series was issued to me in 1918. Beryllium will probably first come into commercial use as an alloy with aluminum. It will likely be many years before the element itself will be used to any great extent, except for specific purposes which will stand a fair cost.

Apart from zinc, beryllium is perhaps the only metal, which, when added in high percentages to aluminum has little effect on the ductility. Within the past few months many alloys of beryllium and aluminum have been prepared by us; some contained as much as 33 per cent beryllium. These alloys are much lighter than aluminum, and can be rolled or drawn with equal ease.

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, Mr. S. Skowronski in the Chair.

AN ATTEMPT TO ELECTROPLATE TUNGSTEN ON IRON.[1]

By C. A. Mann[2] and H. O. Halvorsen.[2]

Abstract.

Salts of tungsten in which the metal occurs as anion are desirable for electrolysis. Such a salt can be supplied to a cell by electrolytic corrosion of a tungsten anode. This was accomplished by using both aqueous and non aqueous electrolytes containing hydrogen chloride or alkali chlorides, but on electrolysis only an oxide of tungsten was obtained on the cathode. In some cases the resistance of the cell was too high to conduct sufficient current. A fused bath of lithium chloride gave proper conductivity, the tungsten anode corroded to form tungsten chloride, and a deposit of metallic tungsten was obtained on the iron cathode.

Most of the early work on the electrodeposition of tungsten concerned itself with the production of a pure tungsten metal, and not with the character or usefulness of the tungsten for electroplating. Because of the excellent resistance of tungsten to acids, except to a mixture of nitric and hydrofluoric, and particularly to sulfuric acid[3] even at a temperature of 200° C., this material would be valuable for chemical equipment were it not for its high cost and the difficulty of making suitable shapes. With the possibility of obtaining a satisfactory electroplated deposit on iron or steel, a variety of equipment resistant to acid action could be cheaply constructed.

In this investigation an attempt has been made to produce a satisfactory electroplate of tungsten on iron, and to study the

[1] Manuscript received July 3, 1923.

[2] Division of Chemical Engineering, Univ. of Minnesota, Minneapolis, Minn.

[3] Desi, J. Am. Chem. Soc. 19, 215.

behavior of tungsten under different electrolysis conditions. It presents only a preliminary study of this subject.

Koerner[4] in a paper published in 1917 after reviewing the early efforts of investigators makes the statement that up to 1909 "no satisfactory method had been developed for the electrolytic deposition of tungsten, and no metallic tungsten had been obtained by electrolysis." Koerner determined that in alkaline solutions, tungsten occurs as the anion, but in acid solutions it occurs as the cation. Koerner also claims that tungsten hexachloride, anodically formed, and tungstic acid both hydrolyze to form $W(OH)_6$, the latter being soluble in solutions of H_2SO_4, HCl, and HNO_3; and that $W(OH)_6$ is ionized to W ions and OH ions and therefore is an electrolyte. From $W(OH)_6$ as an electrolyte in which the tungsten is a cation it should be possible to obtain metallic tungsten, but Reck[5] obtained only an oxide at the cathode by using an acid aqueous solution of $(NH_4)_2WO_4$ and Na_2WO_4. Tungsten sulfide (WS) which is soluble in water has the tungsten as the cation, but on electrolysis Reck obtained only an oxide on electrodes of various metals.

Up to the present time none of the attempts at electrodepositing tungsten appear to have been satisfactory, and at best only tungsten bronzes or the oxides were obtained at the cathode.

Tungsten chlorides, which contain the metal as the cation and which are soluble in several non-aqueous electrolytes, seemed to us to be the most suitable salts to use. The chlorides can be prepared by the direct action of gaseous chlorine on metallic tungsten, but this must be done in the absence of oxygen and moisture the presence of which makes the procedure difficult. Koerner[4] has shown that chlorine will attack tungsten anodically to form the chlorides. This method was used to prepare the electrolyte.

EXPERIMENTAL.

The work was divided into three parts:

A. Use of electrolyte containing oxygen as hydroxyl.

B. Use of pyridine as an oxygen free non-aqueous electrolyte.

C. Fused lithium chloride as electrolyte.

[4] Koerner, Trans. Am. Electrochem. Soc., **31**, 221-247 (1917). This paper contains a detailed account of the work of early investigators.

[5] Reck. "An Attempt to Electroplate with Tungsten," a thesis filed at the School of Chemistry, University of Minnesota (1921).

In all of the experimental work the anode consisted of a plate of tungsten metal and the cathode of a sheet of iron. The work was carried out in glassware except when the fused electrolyte was used, in which case an iron or platinum crucible was employed.

A. Use of an electrolyte containing oxygen as hydroxyl.

Though former investigators have electrolyzed a solution of WCl_6 in absolute alcohol without obtaining metal at the cathode no one seems to have studied the anodic corrosion with chlorine for producing tungsten chlorides under changing conditions of moisture content of the electrolyte, nor the effect of such moisture on the character of the deposit. In the following experiments the electrolytes varied from an aqueous solution of HCl, to a solution of dry HCl gas in absolute alcohol. Both the anode of tungsten and cathode of iron were thoroughly cleaned by grinding and the use of acids.

Experiment No. 1. On applying a potential of 10 volts to a cell containing normal aqueous hydrochloric acid as electrolyte, a current flowed but momentarily and then dropped to zero. An increase of potential to 25 v. caused no further flow of current. A light brown film formed on the anode, which made the tungsten passive. This is in agreement with the suggestions made by Koerner that the WCl_6 with water forms $W(OH)_6$ and 6HCl. As tungsten is unaffected by HCl chemically, it is reasonable to assume that during the time the current did flow that the chlorine ion attacked the tungsten to form some chloride of tungsten.

Experiment No. 2. When 50 cc. of absolute alcohol were added to 50 cc. of normal HCl the same results were obtained as in Experiment No. 1.

Experiment No. 3. The electrolyte used was prepared by passing dry HCl gas into 96 per cent alcohol. With 10 v. a small current flowed which fell off slowly to zero. An increase of voltage to 25 v. caused no further flow of current. Again the anode was coated with a light brown film.

Experiment No. 4. With an electrolyte made by saturating absolute alcohol with HCl gas dried by passing through concen-

trated sulfuric acid, calcium chloride and phosphorus pentachloride, a current of 0.04 amp. per sq. cm. of cathode surface was maintained for two hours when applying an e.m.f. of 5.6 v.

A light brown, loose deposit formed on the cathode, probably some tungsten oxide, but no oxide film formed on the tungsten anode, nor was free chlorine liberated. This indicated that the tungsten was corroded anodically to form a chloride which is soluble in the absolute alcohol, and because of the absence of moisture this chloride did not hydrolyze to form $W(OH)_6$, at least not enough to form an oxide film on the anode. This would explain why the current continued to flow. There is no question about a chloride forming, because the solution in the neighborhood of the anode turned a deep yellow and finally the yellow diffused throughout the bath.

It would seem that under the conditions of the experiment that the tungsten in solution occurs as the cation, and that metallic tungsten should be deposited instead of an oxide. This may, however, take place as follows:

$$C_2H_5OH + HCl \leftrightarrows C_2H_5Cl + H_2O$$

$$H_2O + WCl_x \leftrightarrows WCl_{(x-2)}\,O + 2HCl$$

or

$$2C_2H_5OH + WCl_x \leftrightarrows 2C_2H_5Cl + WOCl_{(x-2)} + H_2O$$

The $WOCl_{(x-2)}$ might ionize as follows:

$$WOCl_{(x-2)} \leftrightarrows WO^{(x-2)+} + (x-2)\,Cl^-$$

and the $WO^{(x-2)+}$ would be the cation.

Similarly tungstic acid or alkali tungstates in acid solution may be considered as forming $W(OH)_6$, and this by dehydration may contain the following cations:

$$W(OH)_6 \rightarrow WO(OH)_4 + H_2O \rightarrow WO^{4+} + 4OH$$

or

$$W(OH)_6 \rightarrow WO_2\,(OH)_2 + 2H_2O \rightarrow WO_2^{2+} + 2OH$$

However, with moisture present as is the case in the preceding experiments, the WCl_x as formed at the anode would undoubtedly

hydrolyze completely to give the $W(OH)_x$ film on the anode, which by making it passive would prevent further formation of WCl_x.

Experiment No. 5. Using the same electrolyte as in the preceding experiment, and with a current of 0.02 amp. per sq. cm. of cathode surface for one hour, a light brown deposit was again obtained at the cathode, which protected the underlying iron when immersed in HCl solution. No gas was evolved at the anode, and the solution became yellow showing the presence of a tungsten chloride. Even with the deposit, the cathode weighed slightly less than in the beginning, due no doubt to the action of the HCl on the iron before a deposit had formed.

When the flow of current was continued for 2.5 hr. the cathode increased in weight and showed a uniform deposit of the oxide of tungsten.

Experiment No. 6. Under the conditions of Experiment No. 5 the hydrogen liberated at the cathode was unable to reduce the oxide to the metal. As the reducing power of hydrogen increases with its solution pressure, and as the solution pressure or overvoltage increases with the lowering of the temperature,[6] Experiment No. 5 was repeated, but the electrolyte was kept at a temperature of 0° C. by surrounding the cell with a freezing mixture. A light brown deposit only was obtained on the cathode, showing the ineffectiveness of the hydrogen to reduce the oxide.

The facts that chlorine does not come off at the anode, that the color of the electrolyte changes, and that a deposit of an oxide of tungsten appears on the cathode, all indicate that the tungsten has been attacked anodically by the chlorine to form a chloride of this metal. When, however, an electrolyte is used which has an appreciable hydroxyl ion concentration, as is the case when moisture is present, the chloride hydrolizes as it is formed at the anode, making the anode passive almost instantaneously. For electrolytes which have a negligible hydroxyl ion concentration, as is the case when absolute alcohol is used, the chloride dissolves and a deposit of oxide of tungsten is obtained at the cathode.

It is the intention of the authors to continue this work with

[6] Allmand, "Principles of Applied Electrochemistry" Chap. 9, p. 132 (1920).

other non-aqueous electrolytes containing hydroxyl groups, as well as those containing oxygen in various forms, but for the present it seemed desirable to try non-aqueous electrolytes which contain no oxygen whatsoever. Because of the excellent solvent properties of pyridine, and because it is an ionizing medium free from oxygen, it was used for experiments under caption B.

B. Use of pyridine as an oxygen free non-aqueous electrolyte.

In the following experiments a tungsten metal anode and an iron cathode were again used, but the electrolyte consisted in one

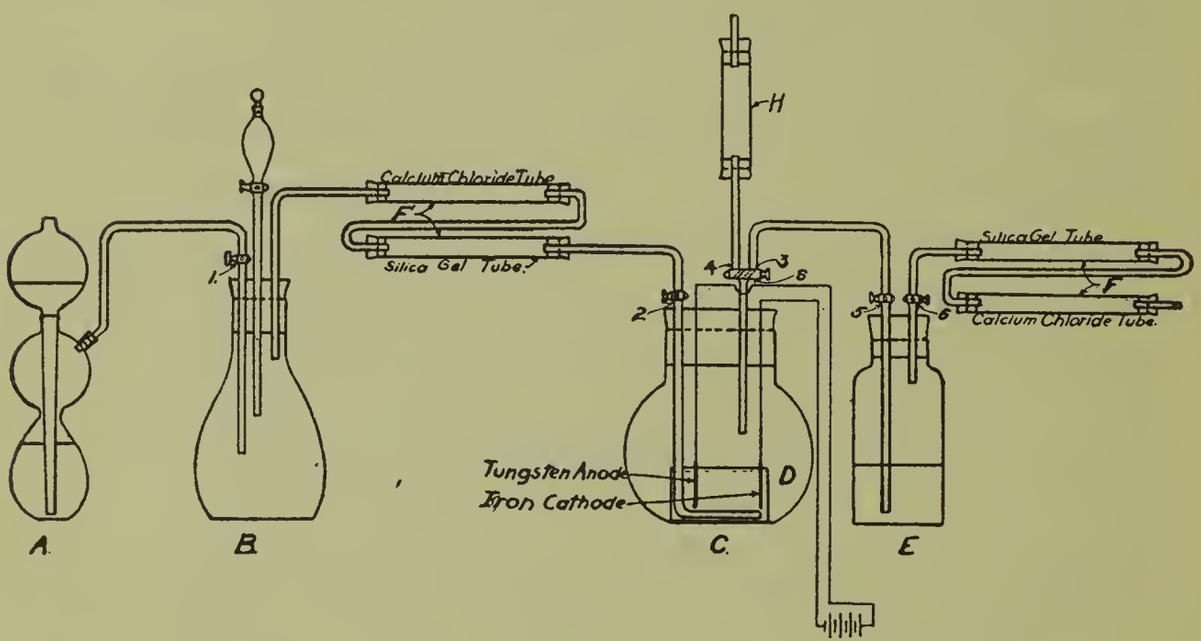

FIG. 1

case of dry HCl gas in anhydrous pyridine and in the other of dry fused LiCl in anhydrous pyridine.

Preparation of dry Pyridine: To one volume of crude pyridine was added two volumes of water and the mixture fractionally steam distilled. The fraction boiling at 94.5° C. was treated with solid sodium hydroxide, when a solution of sodium hydroxide settled out with the pyridine on top. The pyridine layer was repeatedly treated with fresh solid hydroxide until no further layer of sodium hydroxide solution resulted after standing for one week. This dried pyridine was refluxed over anhydrous barium oxide for 2 hr. and then distilled, keeping the moisture from the pyridine by using tubes containing calcium chloride. The dried pyridine was then fractionated and the fraction boiling from 114-115°

C. was used for the following experiments. Only 250 cc. of dry pyridine were obtained from 3 L. of crude pyridine.

Experiment No. 7. The electrolyte was prepared by passing dry HCl into the anhydrous pyridine for 30 min. Using a tungsten anode and an iron cathode a current of 0.01 amp. per sq. cm. under a pressure of 10.4 v. was allowed to flow for 1 hr. The solution turned a bluish green and a dark brown deposit (an oxide of tunsgten) was formed on the cathode. No attempt had been made to protect the electrolyte from the moisture of the air. The hydrogen chloride took up moisture from the air, and under these conditions we might expect the deposition of tungsten oxide at the cathode because of the presence of hydroxyl ions.

In order to carry on the electrolysis out of contact with moisture or oxygen, a closed system had to be used. Fig. 1 shows a diagram of the set-up used, in which A is a hydrogen generator; B, a hydrogen chloride generator; C, a cell container; D, a glass crystallizing dish for the electrolyte and electrodes; E, a bottle of anhydrous pyridine; F and F′, drying columns containing calcium chloride and anhydrous silica gel as shown; and H, a column containing calcium chloride.

The apparatus was first flushed out with dry hydrogen by opening stopcocks 1, 2, and 4 on the two-way cock (s), and allowing the hydrogen to flow for 2 hr. The right amount of anhydrous pyridine was then forced into the cell (D) by closing 4 and opening 3 of stopcock (s), opening 5 and 6, and applying air pressure through the drying tubes F. After closing 5, 6, and 3 again and opening 4, hydrogen was bubbled through the pyridine for 1 hr. to remove any possible absorbed oxygen. Stopcock 1 was then closed and the hydrogen chloride generator (B) was started, using dry salt and concentrated sulfuric acid. The calcium chloride tube H prevented moisture from entering through (4) and acted as an outlet for the excess HCl gas. Connections with the electrodes were made by drawing the wires through the rubber stopper of the container (C).

Experiment No. 8. Two runs were made with this apparatus, using electrodes of 4 sq. cm. area. As soon as the hydrogen chloride generator was started, readings were taken of the time, voltage and amperage. The concentration of the hydrogen chlo-

ride in the pyridine increased with time, until at last the entire solution solidified as pyridine hydrochloride. Table I shows the results obtained from one of the runs, the other being similar.

TABLE I.

Change of Conductivity with Time

Time		v.	Current Density Amp. per sq. dm.
Hr.	Min.		
	0	10	0.00
	15	25	0.50
	30	25	0.25
	45	35	0.25
1	00	40	0.25
1	30	50	0.25
2	00	50	0.00
2	15	110	0.50

In each of these experiments the readings indicate that the resistance of the cell increased with time. This may be due to polarization or to a decrease in ionization. Pyridine hydrochloride increases as the hydrogen chloride is added, thus making the ratio of pyridine to the hydrochloride less. It may be that under these conditions the smaller amount of pyridine does not ionize either the pyridine hydrochloride or the hydrogen chloride to as great an extent as before. No change could be seen on the electrodes nor had the anode decreased in weight. Dry hydrogen chloride did not seem to ionize sufficiently in the anhydrous pyridine to make the system of any value even at high voltages.

Experiment No. 9. As pyridine did not ionize the hydrogen chloride sufficiently, it was thought possible to use some other chloride that would ionize.

Such a chloride to be used must have the following properties: It must be soluble in pyridine. It must furnish chlorine ions in the solution. The anion must contain no combined oxygen, and its cation must have a discharge potential above that of the tungsten ion. One of the few salts that answer these requirements is lithium chloride.

This run was made in the same apparatus as experiment No. 8,

except that the hydrogen chloride generator was eliminated. The dry, fused lithium chloride was placed in cell (D) before sealing the apparatus. The apparatus was flushed out with dry hydrogen, and the pyridine introduced as in the two former runs.

With this solution as the electrolyte a milliammeter would not register the flow of current at any voltage from 0 to 75. This is contrary to the results obtained by Gorski[7], Levi and Voghera[8], and Patten and Mott[9], who state that LiCl in anhydrous pyridine will conduct the current and deposit metallic lithium on the cathode. However, Patten and Mott state "that an extremely small quantity (about 0.1 per cent) of moisture will cause the solution to act upon the lithium, with the formation of an insulating film upon the cathode of sufficient resistance to interrupt the electrolysis."

If this explanation is true, it is difficult to understand why in the preceding experiment, when dry HCl was used instead of the dry fused LiCl, the resistance of the bath increased with time, unless it is due to a hydrogen film on the cathode. If electrolysis had proceeded to the extent of depositing a film of H_2, the chlorine liberated at the anode should have reacted with the material of the anode to produce a chloride in solution, but none was formed nor had the anode lost any weight. Moreover it is of interest to note that in experiment No. 7 where the electrolyte of dry HCl gas in anhydrous pyridine was exposed to the atmosphere, from which it could take up moisture, that the electrolyte did conduct the current, the tungsten anode was acted on by the anodic chlorine to form the chloride soluble in pyridine, and that the tungsten oxide was deposited on the cathode. It is an incontrovertible fact that a cell containing LiCl in pyridine has a high resistance, and the authors feel that this may be due to polarization, particularly because of the tungsten anode, but they are unwilling to attribute the high resistance to imperfectly dried pyridine or LiCl.

C. Use of fused lithium chloride as electrolyte.

As there were no other liquids available which contained no oxygen or chlorine, and yet would be likely to dissolve and ionize

[7] Gorski, Z. für Electrochem. 4, 292 (1897).
[8] Levi and Vogher, Gazz. Chem. Ital. 35, 277 (1905).
[9] Patten and Mott, J. Phys. Chem. 12, 49 (1908).

either hydrochloric acid or alkali chlorides, the attention of the authors was drawn toward the use of fused chlorides as electrolyte. Of these, lithium chloride answers the purpose better than any other, because it has the lowest melting point (600° C.) of any of the chlorides whose cation is high in the electromotive series. A low melting point is desirable, because of the possible volatilization or decomposition at high temperatures of tungsten chloride, which might form anodically. In connection with the use of fused baths, Koerner[4] states that "The electrolysis of molten baths of halogen or oxy-halogen compounds of tungsten is not feasible, as these compounds are not very conductive." The fused lithium chloride, however, may be expected to ionize the tungsten chlorides and thus furnish a satisfactory electrolyte.

Experiment No. 10. In this experiment the lithium chloride was kept molten by a gas flame placed directly under the container, which was an iron crucible. An anode of tungsten and a cathode of iron were used. Three runs were made, using the same bath of lithium chloride, but introducing fresh electrodes. The bath continually increased in WCl_x. The connections were made on the electrodes by cutting a slot into a small steel rod and forcing the electrodes into this slot. Results are tabulated in Tables II, III, and IV.

TABLE II.

Change of Conductivity with Time and Increase of WCl_x.

Time in Min.	v.	Current Density Amp. per sq. dm.
00	1.0	4.77
5	0.7	3.50
10	0.6	3.50
15	0.5	3.00
20	0.5	3.00
25	0.5	2.50
30	0.4	2.50
35	0.4	2.50

A very dark spongy soft deposit was formed on the cathode in run No. 1. This was probably due to too high a current density, which is commonly responsible for spongy metallic deposits.

In run No. 2 a dark spongy deposit was formed, as in the

experiment recorded in Table I. This also was probably due to too high a current density.

The deposit was lighter in color in run No. 3, and not so spongy as in runs No. 1 and No. 2. The current density was still too high.

TABLE III.

Change of Conductivity with Time and Increase of WCl_x.

Time in Min.	v.	Current Density Amp. per sq. dm.
00	1.20	5.00
5	0.70	3.50
10	0.60	2.50
15	0.40	2.50
25	0.35	2.50
30	0.35	2.50
40	0.35	2.25
45	0.35	2.25

TABLE IV.

Change of Conductivity with Time and Increase of WCl_x.

Time in Min.	v.	Current Density Amp. per sq. dm.
00	0.9	5.50
5	0.5	3.00
10	0.4	2.50
15	0.35	2.50
25	0.30	2.25

Experiment No. 11. Believing that the high current density was the cause of the other spongy deposits, another run was made with the same lithium chloride containing the chlorides of tungsten, using a cathode area of 4 sq. cm. under the conditions given in Table V.

The loss of weight of the anode was 0.1380 g. The gain in weight (0.0013 g.) of the cathode does not represent the actual weight of the deposit, as the lithium chloride had first corroded the iron. This was evidenced by a sediment at the bottom of the crucible, which proved to be iron oxide. The iron may have gone into solution as a chloride of iron, that oxidized at the surface of the electrolyte to the oxide of iron. This was indicated by a test

for iron in the lithium chloride. Some of this iron may have come from the crucible.

TABLE V.

Change of Conductivity with Time.

Time		v.	Current Density Amp. per sq. dm.
Hr.	Min		
	00	0.20	1.25
	15	0.22	1.11
	45	0.22	1.11
1	15	0.22	1.11
1	30	0.20	1.00
1	45	0.20	0.90
2	00	0.20	0.75
2	15	0.20	0.75

A qualitative test showed the presence of tungsten in the lithium chloride bath.

A light grey metallic plate was formed on the cathode, which gave a qualitative test for tungsten. The test for tungsten was made in the following way[10]. The cathode was put into fused sodium carbonate, and allowed to remain there thirty minutes. The sodium carbonate was then dissolved in water and was neutralized with hydrochloric acid, and finally an excess of the acid was added. Upon placing a piece of metallic tin in the solution, if tungsten were present a blue color would appear. This test was tried on metallic tungsten and it was found to work satisfactorily.

Amp. hr. used, 0.1131.

Loss in weight of tungsten, 0.1387 g.

Faradays per gram atom of tungsten =

$$\left(\frac{3600}{96500} \times 0.1131 \times 184\right) \div 0.1387 = 5.60$$

The tungsten evidently dissolved as the hexavalent ion. If the current efficiency were 100 per cent, hexavalent tungsten should require 6 Faradays per mole. The difference between 5.60 and 6 is probably due to the solubility of W in fused LiCl. Also, the pentachloride may have formed instead of the hexachloride with low current efficiency.

[10] Hartman, Chem. Eng. 23, 244-50 (1916).

Experiment No. 12. The purpose of this experiment was to ascertain whether the iron had been corroded, and to measure the drop in voltage across the cell on open circuit. If a plate of tungsten is produced at the cathode, using a tungsten anode, the potential drop across the cell on open circuit should decrease and approach zero.[11]

The run was made in a platinum crucible instead of one of iron, using a fresh batch of lithium chloride. Using a current density of 0.5 amp. per sq. dm. of cathode surface for 2 hr., the loss of weight of the anode was 0.0175 g. and the cathode also showed a loss in weight of 0.0824 g. The potential drop across the electrodes on open circuit is shown in Table VI.

TABLE VI.

Change of Potential Drop Between Electrodes with Time of Deposition.

Time		v.	Current Density Amp. per sq. dm.	Potential Drop in Volts on Open Circuit
Hr.	Min.			
	00	0.15	0.50	0.10
	5	0.15	0.50	0.08
	20	0.18	0.50	0.08
	35	0.20	0.50	0.09
	50	0.12	0.50	0.05
1	5	0.12	0.50	0.04
1	20	0.10	0.50	0.03
1	25	0.10	0.50	0.02
1	50	0.10	0.50	0.02
2	00	0.10	0.50	0.02

A light grey metallic plate was produced at the cathode that gave a qualitative test for tungsten. A test also showed the presence of tungsten in the lithium chloride.

Amp. hr. used, 0.04.

Loss in weight of the tungsten, 0.0824 g.

Faradays per gram atom of tungsten =

$$\left(\frac{3600 \times 0.04 \times 184}{96500}\right) \div 0.0824 = 3.32$$

[11] Allmand, "Principles of Applied Electrochemistry," p. 9 (1920).

Possibly at lower current densities the tungsten dissolves as an ion of lower valence, probably as the tetravalent ion in this case. At 100 per cent current efficiency the tetravalent tungsten should require 4.00 Faradays per mole. The difference between 4.00 and 3.32 may be due to the solubility of W in fused LiCl.

The loss of weight of the cathode indicates that the lithium chloride corrodes the iron. This was confirmed by a test for iron in the lithium chloride. The fact that the electrode showed a loss in weight in this experiment, and a gain in weight in experiment No. 11, can be explained on the basis that the former run extended over 3 hr., whereas this one over only 2 hr., and that the former run was made at twice the current density.

TABLE VII.

Change of Potential Drop Between Electrodes with Time of Deposition.

Time		v.	Current Density Amp. per sq. dm.	Potential Drop in Volts on Open Circuit
Hr.	Min.			
	00	0.2	0.50	0.10
	15	0.5	0.50	0.30
	30	0.10	0.50	0.05
1	00	0.15	0.50	0.07
1	30	0.15	0.50	0.07
1	45	0.10	0.50	0.02
2	00	0.08	0.50	0.01

The decrease in the potential drop and its approach towards zero is an indication that the final cell was W : LiCl : W, which should have no potential drop on an open circuit. This open circuit drop may be due to difference in concentration around the electrodes because of a slow rate of diffusion through the molten bath.

Experiment No. 13. The purpose of this experiment was to verify the observations made on the potential drop on open circuit. This run was also made in a platinum crucible, with the same lithium chloride used in the previous experiment. The results are given in Table VII.

The loss of weight of the anode, which was 0.0820 g. shows that the Faradays required per mole of tungsten is 3.34.

Faradays per gram atom of tungsten =

$$\left(\frac{3600 \times 0.04 \times 184}{96500}\right) \div 0.0820 = 3.34$$

This checks the former result found in experiment 12.

The drop in voltage on open circuit in this case also shows that the tungsten must have been plated on the cathode, which was corroborated by the qualitative test, but no lithium was found in the deposit.

In the last three experiments a light grey metallic plate was obtained on the iron cathode, which gave the qualitative test for tungsten but no lithium. The deposit was firm and coherent, and could be removed only by using emery cloth. This plate resisted the action of concentrated hydrochloric acid when immersed in it for an extended period of time.

This investigation will be continued using other non-aqueous electrolytes such as oxygenated, chlorinated and nitrogen containing compounds, as benzonitrile, aniline, quinoline, liquid anhydrous HF, as well as on molten electrolytes.

SUMMARY AND CONCLUSION.

This investigation has brought out the following points:

1. When the hydroxyl ion concentration is relatively high in an electrolyte, tungsten will not dissolve anodically because of the formation of electrically resistant oxide film.

2. When the hydroxyl ion concentration is very low, tungsten will be dissolved at the anode by the chlorine ion.

3. In the presence of any hydroxyl ions a complex tungsten oxygen ion will be deposited in the form of some oxide of tungsten at the cathode.

4. Dry pyridine will not ionize hydrogen chloride or lithium chloride sufficiently to allow a current to flow even at high voltages. The slightest trace of moisture increases ionization, and allows the current to pass with an oxide deposit at the cathode.

5. Using fused lithium chloride as an electrolyte, tungsten will be dissolved anodically and will deposit upon the cathode as metallic tungsten.

6. At high current densities a spongy burnt deposit results.

7. When tungsten dissolves anodically in lithium chloride, the Faradays required per mole of tungsten dissolved depends upon the current density.

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DISCUSSION.

MENAHEM MERLUB-SOBEL[12]: The relative ease with which oxides of tungsten are reduced by hydrogen makes it seem all the more remarkable that the faintest trace of hydroxyl ion, as claimed by Messrs. Mann and Halvorsen, should prevent the reduction of tungsten to the metallic state. Is it not possible that the black coating hitherto considered as an oxide of tungsten, WO, is actually a very fine deposit of tungsten powder which, because of its physical structure, is of poor conductivity?

In this connection, an experiment using an electrolyte where the absolute absence of hydroxyl is assured has proven interesting. Tungsten hexachloride is very soluble in *phosphorus oxychloride,* and may be expected to ionize somewhat in the latter medium. The oxychloride of phosphorus is, as is well known, absolutely incompatible with water, decomposing immediately into gaseous HCl and meta-phosphoric acid, so that hydroxyl ions are impossible in $POCl_3$ solution. Electrolysis of tungsten hexachloride in such a phosphorus oxychloride solution, using a current density of two amperes per square decimeter on a gold cathode, did not yield a bright tungsten plate, but gave, rather, a black deposit similar to that obtained in aqueous solutions. There being no hydroxyl present, the plate or coating is probably not WO, since it is difficult to conceive that metallic tungsten, so low in the elec-

[12] Columbia University, School of Chemical Engineering. Tests carried out under the direction of Dr. Fink.

tromotive series, should be a sufficiently powerful reducing agent to decompose the very stable phosphorus oxychloride, a compound in which the oxygen is held very firmly.

In none of the author's statements, involving the use of fused lithium chloride, had the voltage risen above 1.2, while the maximum on the three runs where a good metallic plate was obtained was only 0.5 volt, ranging from that point down to 0.08 volt. The theoretical decomposition voltage of lithium chloride is probably no less than 3 volts; by use of Kelvin's rule (correcting the heat of reaction for the difference between room and fusion temperature) this voltage comes to be 4.04 volts. Even though Kelvin's rule is inaccurate to a considerable extent, the formation of metallic lithium under practical conditions with base-metal electrodes is extremely unlikely under 3 volts.

In this regard, an experiment using an eutectic mixture of KCl and LiCl (theoretical melting point 358° C.) did show a marked change as the impressed e. m. f. was raised to above four volts; there was visible evolution of gas at the anode, and the cathode, when washed with water prior to polishing, gave unmistakable evidence of the presence of an alkali metal in the deposit by evolution of gas bubbles which even caught fire once.

On the other hand, if lithium had formed, it would not have volatilized from the bath unless the lithium chloride were itself kept at its boiling temperature. Lithium has the highest vaporization point of all the alkali metals, over 1,400° C., while the LiCl itself vaporizes at a lower point, 1,382° C. Unless the temperature were deliberately raised to about 1,300° C. (and the experimenters' choice of LiCl as being the lowest-melting available salt gives the impression that they kept the temperature of the fused electrolyte as low as possible) it is hard to conceive that any metallic lithium might have volatilized from the cathode. Finding no lithium metal in the deposit is therefore only further indication of its non-formation under low e. m. f.

If, then, high temperatures are not needed in order to volatilize off any alkali metal formed, the next logical step is to attempt to lower the temperature of the fused bath. Advantages of lower-fusing baths are: (1) More easily obtained and maintained constant. (2) Less danger of loss of tungsten chlorides by volatilization. (3) Higher current densities available without

"burning" the deposit (the very low current densities found necessary by Messrs. Mann and Halvorsen may be due to the high temperature at which they had to work). (4) Less corrosion of crucibles. In regard to the last, it should be remembered that the chief difficulty in the direct electrolysis of fused NaCl to metallic sodium, as in the Acker cell, is the inability to find materials adequate to withstand the corrosive action of NaCl at its high fusion temperature, 800° C.

None of the chlorides of the alkali or alkaline-earth metals (with the exception of the rare $GlCl_2$) have a lower fusion point than has lithium chloride, but eutectic mixtures of various chlorides are obtainable which have considerably lower melting temperatures than that of LiCl. Of these, the outstandingly low one is the 40.5 per cent KCl-59.5 per cent LiCl (molecular) mixture, with a theoretical fusion point of 358° C.

C. A. MANN (*Communicated*): Mr. Merlub-Sobel suggests "that the black coating hitherto considered as oxide of tungsten, WO, is actually a very fine deposit of tungsten powder, which, because of its physical structure, is of poor conductivity." We have merely taken for granted the statement of Fischer,[13] that a blue-black precipitate forms on the cathode analyzing to show 92.33 per cent of tungsten, corresponding to the oxide, WO.

Because of the incompatability of water with $POCl_3$, Mr. Merlub-Sobel suggests an electrolyte of tungsten hexachloride in $POCl_3$. He too obtained a black powder on a gold cathode. If this work was carried out in the presence of air there is no reason why the tungsten hexachloride should not also be hydrolyzed by the moisture of the air to form a tungsten oxychloride, thus supplying tungsten oxide cation, which would deposit on the cathode. In our own experiments, the fact that the decomposition voltage of the lithium chloride had not been reached is the real explanation of the absence of the lithium metal.

[13] Trans. Am. Electrochem. Soc., 31, 223 (1917).

A paper presented at the Forty-fifth General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 26, 1924, President A. T. Hinckley in the Chair.

CLEAR FUSED QUARTZ MADE IN THE ELECTRIC FURNACE.[1]

By Edward R. Berry.[2]

Abstract.

The art of making fused quartz dates back to 1839, but it is only during the last 23 years that the development of clear fused quartz has made rapid progress. A new method for making various clear quartz shapes is described. The important steps in the process included a preliminary fusion in an electric vacuum furnace, followed by a second fusion in an electric pressure furnace. The furnaces are of the resistor type. Various applications of the new product, such as moving picture apparatus lenses, mirrors in reflecting telescopes, thermometers, tuning forks, etc., are described. [C. G. F.]

INTRODUCTION.

It is the purpose of this paper to present some of the recent results of the development of clear fused quartz, and to focus attention on some of the properties of this material, which are surprising even though they may not be entirely new. The art of making fused quartz dates back to 1839, when Gaudin in France discovered the characteristic thermal properties of fused quartz. There have been a number of advances in the art since that date, but most of the development has been concerned with the opaque variety of fused quartz, usually made from sand. It is only during the past twenty-three years that the development of clear fused quartz has made rapid progress.

It has been possible for many years to make fused quartz of a high quality in small sections and lengths, by hand labor in the

[1] Manuscript received February 15, 1924.

[2] Assistant Director, Thomson Research Lab. of the General Electric Co., West Lynn, Mass.

ordinary blast flame, using gas and oxygen. This has been done by piecing together small sections of crystal in the flame, or by adding silica powder from time to time until the piece has grown to the heating limit of the flame, an obviously slow and expensive

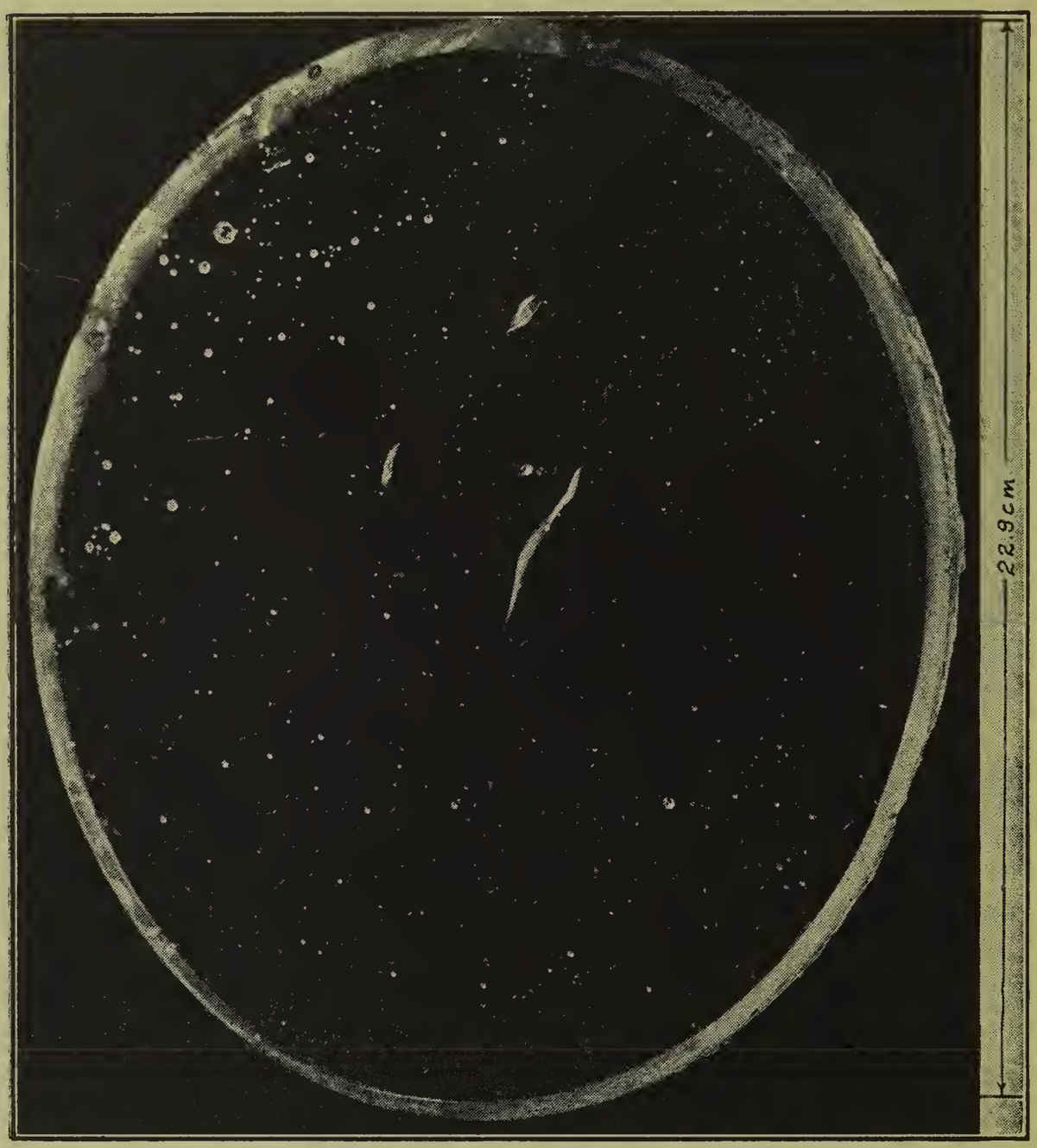


FIG. 1

process. From this step in the development of the art to the point where large masses of equal quality, as shown in the cuts, can be made has been a long one and a difficult one. In the last few years the advances made by the process described in this paper have been so rapid and far-reaching that there seems to be

no limit now to the size of high quality clear fused quartz which can be made, except that which may be imposed by mechanical difficulties.

METHOD OF FUSION.

When it is desired to obtain fused quartz of the quality shown,[3] and which is illustrated in the photographs, it is necessary to start with the highest quality of raw material, of which there is none better than water-clear crystals. It is much more difficult to make fused quartz of this high quality from sand, even if its purity exceed 99 per cent. The rock crystal used in this work besides being water clear, contains probably less than 0.2 per cent impurities. The surfaces are often encrusted with iron oxide and other foreign material, and the crystal itself can be seen to contain clusters of small bubbles. The crystal therefore is washed in acids, and is then broken up and the unsuitable pieces discarded.

There are two distinct steps in the preparation of these tubes, rods, ribbons and cane, the more important of which is the initial fusion. The clean quartz crystal pieces, which are of various sizes, are packed as densely as possible into a graphite or carbon crucible, so that during the cracking of the crystals, which is bound to occur as the temperature is raised, the parts cannot separate and allow small amounts of gas which may be present to enter the many crevices and thus give rise to bubbles. These tightly packed crucibles are placed in a modified vacuum furnace, and the temperature raised as quickly as possible to the melting point. During this fusion the pressure in the furnace is kept as low as possible. The time required for fusion will vary with the conditions, and in all cases no more than 45 min. is necessary.

The energy required for fusion in vacuum is from 3 to 8 kw.-hr. per lb. of quartz, and the loss of quartz due to volatilization is negligible, compared with other charges. The result of this first fusion is a clear, transparent slug, containing comparatively few bubbles, ranging in size from a pin point to 2 or 3 mm. in diameter. Whether these bubbles have been formed by a foreign gas or by silica vapor, it must be remembered that they have been formed at a temperature of about 1800° C., and con-

[3] A large variety of samples made of the new quartz were shown to audience.—Ed.

sequently their pressure at room temperature is very small. This slug is now placed in another graphite crucible, which is suspended in a vertical carbon tube furnace. A graphite piston which just

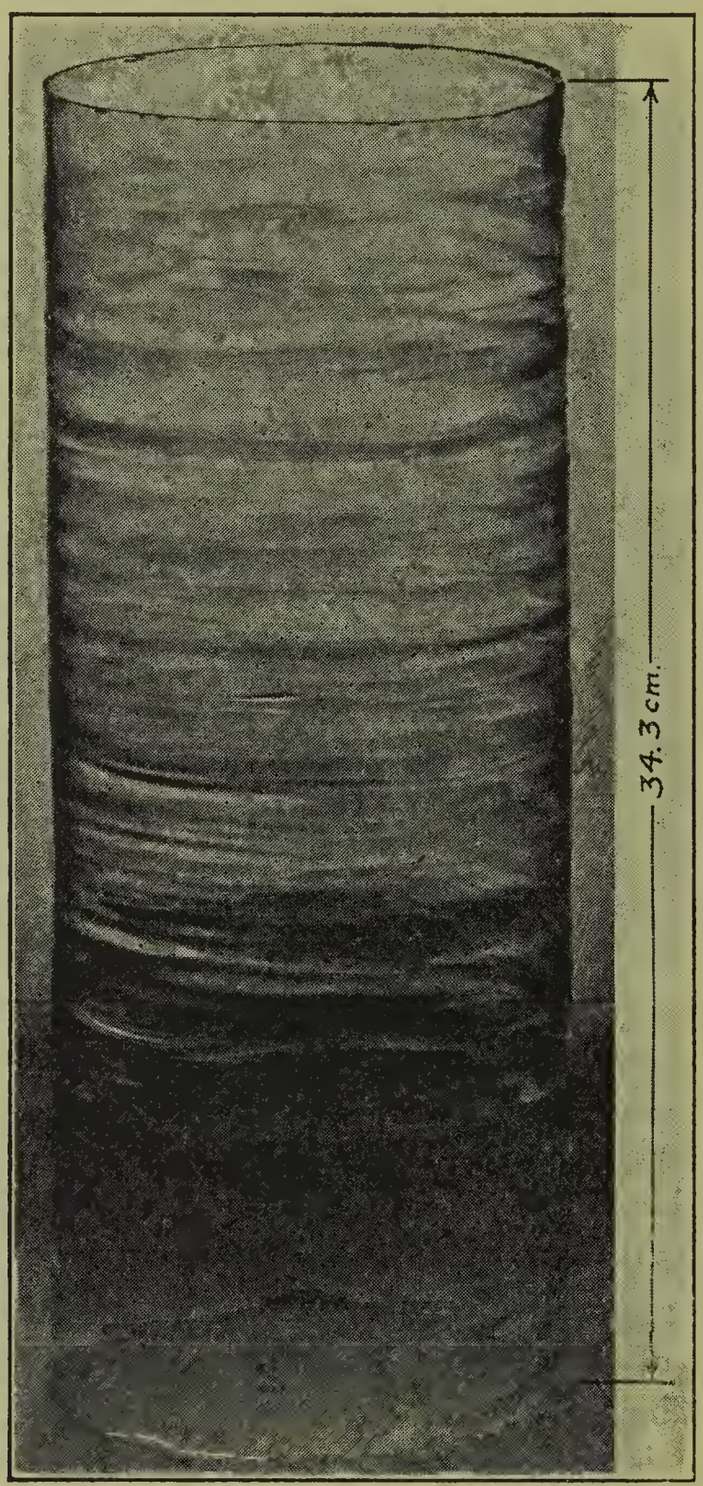


FIG. 2.

fits the crucible is placed on top of the fused quartz slugs, and a weight is placed on top of a plunger attached to the piston. The slugs are again brought to a fusion, the bubbles are largely col-

lapsed, and by the action of the weight the quartz is extruded in various forms, such as rods, tubes, ribbon, etc. This material is practically free from bubbles, but because of limiting dimensions it may become necessary to re-work some of this, which is accomplished by the usual bench methods with an oxygen-illuminating gas flame.

When it is desired to obtain large blocks as free from bubbles as the tubing, cane and ribbon are, a somewhat different operation is necessary. As before, the quartz is fused in a vacuum furnace, which is also designed to withstand very high pressures. As soon as the material is fused, the vacuum valve is closed and the pressure in the tank or furnace is brought up to a pressure depending on the object in view, in less than a minute. This pressure collapses the bubbles and makes it possible to obtain large slugs freer from bubbles than many kinds of the best optical glass.

Previous attempts to reduce the bubbles by continued heating above the melting point resulted, after a certain stage, only in excessive loss of silica by volatilization. We have fused quartz at initial pressures of 600 lb. per sq. in. (40 kg. per sq. cm.) atmospheric pressure, and less than 0.5 mm. of pressure. In the first case the mass was practically opaque, at atmospheric pressure it was considerably improved although much inferior to the present quality of quartz, and under vacuum conditions a large mass can be produced, which from the standpoint of number of bubbles is satisfactory.

Not the least of the difficulties encountered in this development has been that in connection with the furnace equipment. The vacuum furnace in particular had to be greatly changed and enlarged, with the result that we now have probably the largest vacuum furnace in daily use, capable of operating at low pressures. Then in addition to this the furnace had to be so constructed as to withstand repeatedly on the cover a total pressure of over 1,000,000 lb. (460,000 kg.), and of course as the size of the furnace increases these difficulties are multiplied. Special attention must be paid to the design of resistor unit, to the thermal insulation and even heat distribution, to the cooling of the terminals and many other factors presented in the use of these two extremes in pressure.

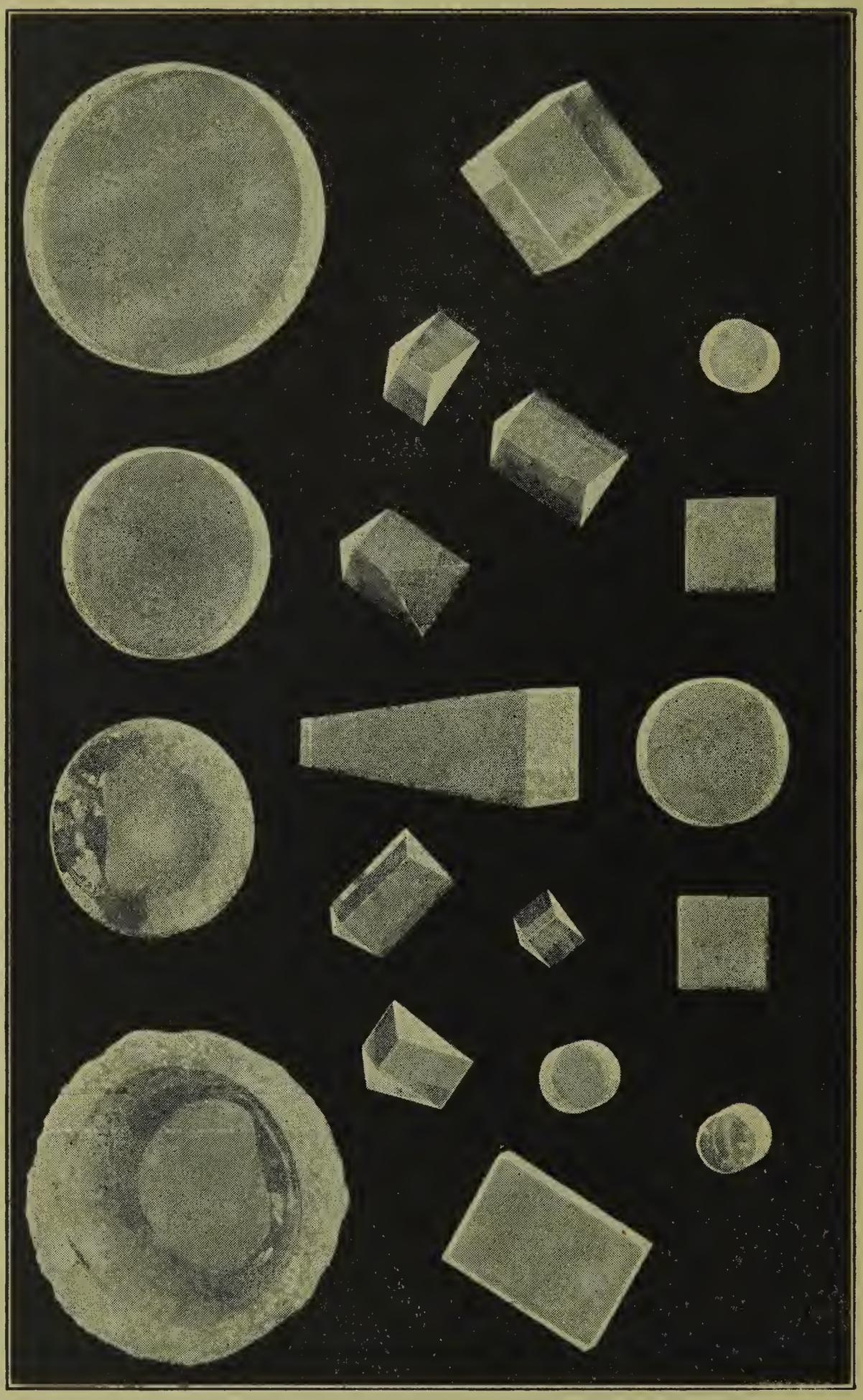


Fig. 3.

When the quartz crystal is heated between 500° and 600° C., it undergoes a remarkable physical change, cracking into small pieces sometimes with explosive violence. This is due to the difference of co-efficient of expansion along the two axes, subjecting the crystal thereby to great strain; and because of decrepitation, owing to the presence of water and liquid carbon dioxide held in vast numbers of minute cavities throughout the crystal. The only advantage, therefore, in using large crystals for fusing lies in the greater ease of keeping the charge free from foreign material before the different particles begin to coalesce.

Hereaus has heated crystal quartz in small pieces, about the size of a nut, very slowly so that no cracking occurs and, consequently, no bubbles are included in the vitreous pieces. Herschkowitsch, on the other hand, has arrived at about the same result by accelerating the heating process so that a film of vitreous material is formed on the outside and prevents air from penetrating to the center, even though cracks may develop. As a matter of fact these processes, while interesting, are subject to very sensitive control and are impractical where large masses are to be fused.

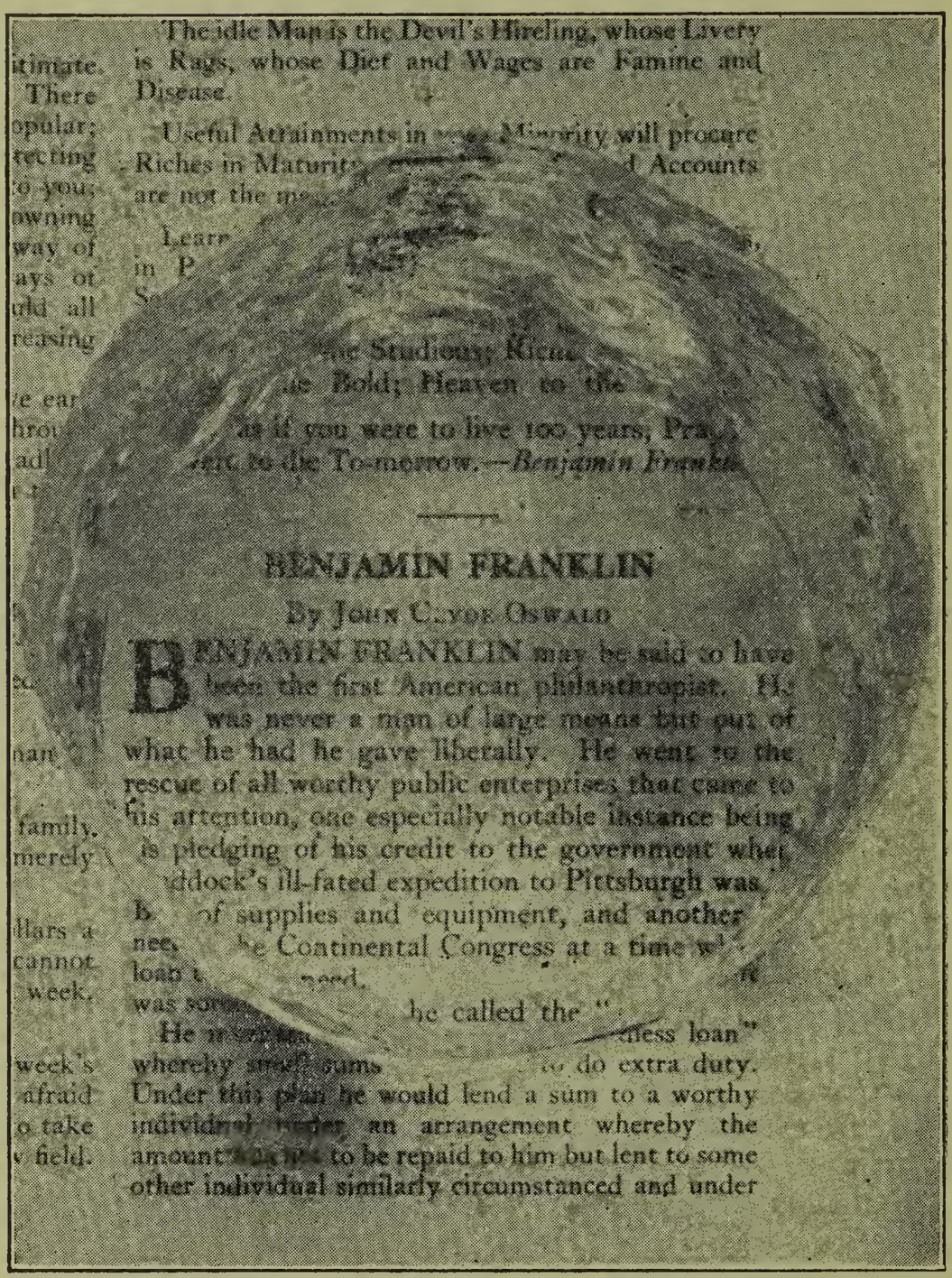
To obtain masses quite free from bubbles, it has been found best to raise the temperature rapidly to 1400° or 1500° C., at which point the pieces begin to coalesce. At about 1750° C. the quartz is thoroughly fused, though it is still viscous. In fact, the viscosity is high, even though the temperature be well over 2000° C. Vaporization of fused quartz is rapid at 1600° C., and at 1750° C. the loss due to evaporation is great. Further increase in temperature results in no great gain in fluidity.

HOMOGENEITY OF FUSED QUARTZ.

The difficulties of obtaining perfectly homogeneous fused quartz free from striæ, strain, bubbles, and double refraction, must be apparent to any one who has worked on this problem, and discouraging perhaps to those who have tried to buy such material. It is a little too early to state in what quantities such a product can be produced, but we have manufactured quartz of this quality which contained only two or three bubbles visible to the eye. This quality, however, has not as yet been placed on a commercial basis.

PROPERTIES AND APPLICATIONS OF CLEAR FUSED QUARTZ.

The fact that for many purposes clear fused quartz can be used up to 1000° C. without injury, that its coefficient of thermal


The idle Man is the Devil's Hireling, whose Livery is Rags, whose Diet and Wages are Famine and Disease.

Useful Attainments in ... Minority will procure ... Riches in Maturity ... d Accounts ... are not the ...

Learn ... in P ... S...

...ne Studious; Rich... ...de Bold; Heaven to the ... as if you were to live 100 years; Pra... ...ers, to die To-morrow.—*Benjamin Franklin.*

BENJAMIN FRANKLIN

By John Clyde Oswald

BENJAMIN FRANKLIN may be said to have been the first American philanthropist. He was never a man of large means but out of what he had he gave liberally. He went to the rescue of all worthy public enterprises that came to his attention, one especially notable instance being ... is pledging of his credit to the government when ...ddock's ill-fated expedition to Pittsburgh was ... B... of supplies and equipment, and another nec... ...he Continental Congress at a time w... loan ... need. ... was sore... ...he called the "... ...ness loan" whereby small sums ... ...o do extra duty. Under this plan he would lend a sum to a worthy individual under an arrangement whereby the amount was not to be repaid to him but lent to some other individual similarly circumstanced and under

FIG. 4.

Print as seen through clear fused quartz cylinder, 7.6 cm. in diameter, 23 cm. long.

expansion is so small as to make it almost negligible, and that it will transmit light rays even into the extreme ultra-violet with very little absorption, gives to it a great utility value, not only to the scientist but to the manufacturer as well.

The specific gravity of clear fused quartz is 2.21; its coefficient of thermal expansion, 58 x 10^{-8}, is about 1/17 that of platinum and 1/34 that of copper; so small that a rod of quartz one meter in length will expand only about 0.6 of a millimeter for 1000° C. rise in temperature. The small probability of fracture under sudden changes in temperature, because of this property, makes it especially desirable for many uses. Furthermore, where it is used as a mirror in reflecting telescopes, this small expansion or contraction with change in temperature causes almost no distortion of the image, and, consequently, much greater accuracy is made possible. This property also makes the grinding of a lens or mirror less tedious and costly, as it is not necessary to await the cooling of the shape in order to get the desired curve. It is possible to heat a tube of clear fused quartz say 5/8 in. (1.6 cm.) in diameter to melting point and plunge it into ice cold water without fracturing.

Its index of refraction for the D line is 1.459, and while its dispersion is higher than optical glass, it is more constant because of the smaller effects due to temperature changes. If the rays which have entered are nearly parallel to a rod of quartz, they are totally reflected internally and on account of this can pass around curves that are not too sharp. This property coupled with a very small absorption loss makes it possible to transmit light through great lengths of curved rod or tubing with very little loss.. A rod of this fused quartz one meter long will emit at one end about 93 per cent of the total visible light passed into the other end. For the better grades of optical glass the highest percentage transmitted under the same conditions is not more than 65 per cent.

The ordinary run of quartz made by this process and used in the fabrication of quartz-mercury arc lamps will transmit light wave lengths as low as the 1850 Å line in the ultra-violet. From the opposite end of the spectrum the heat rays also are transmitted with little loss. For example, if one end of a fused quartz rod 12 in. (30.5 cm.) long is heated to incandescence, it will be found uncomfortable to hold the finger over the other end, although one may comfortably grasp the rod a few inches from the heated zone.

Clear fused quartz is the only known material which can be obtained in quantity, which is transparent to those rays in the ultra-violet, so important not only in the treatment of diseased conditions, but in the maintenance of our general health. It, therefore, occupies a unique position, one which is being recognized more and more by the medical profession.

By the process here described it is now possible to make tubes, rod, ribbon and cane in lengths of 30 ft. (9.2 m.) and in shorter lengths of diameters up to eight inches. Blocks have been made up to 11.5 in. (29 cm.) in diameter and 6 in. (15.2 cm.) thick which have comparatively few bubbles, which are widely separated. Such quartz is comparable in general appearance to the best quality of optical glass. Such material is suitable for prisms, lenses, and for use in instruments where the transmission of invisible and visible rays is an important factor.

Constant progress on this development is being made, and it is hoped that perfect homogeneity can be made the rule rather than the exception. It is expected that for most optical work this quality of the present material will be entirely satisfactory.

Projection Lenses.

Fused quartz lenses 4.5 in. (11.4 cm.) diameter have been for several months successfully operated on test in motion picture projection machines, using currents as high as 150 amp., and where glass lenses cracked almost daily.

Thermometers.

It is well known that in the ordinary glass thermometers there is an appreciable lag in the glass; so that successive readings in a descending scale are inaccurate. To test the extent of this we have placed a standard glass thermometer and a quartz thermometer of our own construction in the same bath and raised the temperature to 515° C. and then lowered it again to 0° C. In this particular case the mercury in the glass came back to four divisions below the zero mark, whereas the mercury in the quartz returned exactly to its original calibrated mark at zero. While the capillary in the quartz tubing is not exactly uniform throughout its entire length, it is so uniform that a calibration of the tube

over its whole length would eliminate any inaccuracies due to the slight non-uniformity.

Tuning Forks.

It is known that as a standard of pitch the tuning fork is about the only appliance in use. As these are of necessity made of hardened steel changes in pitch accompany temperature changes, but what is more important, on account of the work which has to be done in adjusting these steel forks to the desired pitch by grinding or otherwise working them, there are resultant changes in elasticity and dimensions resulting in disturbance of the note of actual pitch. A tuning fork of quartz is not subject to these changes to any appreciable degree.

This work has all been carried on in the Research Laboratory of the General Electric Company at Lynn, Mass., and in presenting this paper I wish to express my appreciation of the efforts of L. B. Miller and P. K. Devers, who, in a large measure, were responsible for the good results obtained.

DISCUSSION.

A MEMBER: What will be the expense of this quartz in comparison with that of glass?

E. R. BERRY: I can best answer that by stating that the conditions are similar to those surrounding the earlier manufacture of bakelite. I recall that at one of these meetings a similar question was asked Dr. Baekeland, and I will make a reply similar to his; that is to say, that the costs of raw material, power and time consumed in the processes of manufacture are all moderate, or even cheap, and that while the development has been very costly, I am convinced that clear fused quartz is eventually going to be produced at prices which will enable one to use it for a multitude of purposes heretofore quite impossible. It should be evident that in ordinary shapes, such as tubing, rod, etc., it will always be much more expensive than glass. For optical purposes I believe

its cost will eventually compare favorably with that of high-grade optical glass.

B. H. JACOBSON[4]: How brittle is this material, compared to similar forms of glass?

E. R. BERRY: About the same as glass, except in heavy masses where, due to lack of strains, it appears to be less brittle than glass.

[4] Charleston, W. Va.

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